Supporting Information

An amino acid based system for CO₂ capture and catalytic utilization to produce formates

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Materials and methods

Unless otherwise stated, all reactions were conducted under an argon atmosphere. Ru-MACHO-BH (Ru-1, Strem, 98%), Ru-MACHO (Ru-2, Strem, 98%), Ru-MACHO\textsuperscript{Pr} (Ru-3, Strem, 97%), L-lysine (TCI, 98%), L-tyrosine (TCI, >98.5%), L-threonine (TCI, >99%), L-methionine (Alfa Aesar, >98%), L-glutamic acid (TCI, >99%), L-serine (TCI, >99%), L-proline (Acros Organics, >99%), L-cysteine (TCI, >98%), L-histidine (Sigma-Aldrich, >99%), L-tryptophan (TCI, >98.5%), glycine (Merck, >99.7%), L-glutamine (TCI, >99%), 1,5-diaminopentane (TCI, >98%), 6-aminohexanoic acid (Alfa Aesar, 99%), 2,3-diaminopropanoic acid (fluorochem, 95%), tetramethylguanidine (Alfa Aesar, 99%), pentaethyleneguanamine (Sigma-Aldrich, >98%), deuterium oxide (Deutero, 99.9%) were purchased from commercial suppliers and used without further purification. Milstein’s Ru-PNP complex (Ru-4)\textsuperscript{1} and Fe-MACHO\textsuperscript{Pr}-BH (Fe-1)\textsuperscript{2} were synthesized according to literature. \textsuperscript{1}H and \textsuperscript{13}C were recorded using Bruker AV 300 MHz and Bruker AV 400 MHz spectrometers. \textsuperscript{1}H and \textsuperscript{13}C NMR chemical shifts were determined relative to the internal standard THF (3.74 ppm and 68.68 ppm respectively) or DMF (7.92 ppm and 165.53 ppm respectively) in D\textsubscript{2}O. \textsuperscript{13}C NMR-quant were performed with relaxation delay = 20s (rd>20s did not change the integration), number of scans = 512, acquisition time = 1.1141s.\textsuperscript{3} Deionized (DI) water was used for CO\textsubscript{2} capture and hydrogenation reactions.

CO\textsubscript{2} capture with amino acids

Capture with CO\textsubscript{2} (2 bar): Amino acid (5.0 mmol) was added in a 25 mL Schlenk tube, followed with 1.0 mL of DI water, then 2 bar of CO\textsubscript{2} was charged into the Schlenk. Afterwards, the Schlenk tube was closed and stirred at r.t. for 2-18 h. The captured CO\textsubscript{2} amounts were calculated by gravimetric analysis.
Table S1. CO₂ capture with amino acids under 2 bar of CO₂.

| Entry | AA [5 M] | Time [h] | Captured CO₂ [mmol][a] | CO₂/AA[b] |
|-------|----------|----------|-------------------------|-----------|
| 1     | H₂N–O    | glycine  | 2                      | 0.47      | 0.09      |
|       |          |          | 18                     | 0.47      | 0.09      |
| 2     |        | L-proline| 2                      | 0.39      | 0.08      |
|       |          |          | 18                     | 0.40      | 0.08      |
| 3     |        | L-methionine| 2                  | 0.27      | 0.05      |
|       |          |          | 18                     | 0.28      | 0.06      |
| 4     |        | L-tyrosine| 3                      | 0.45      | 0.09      |
|       |          |          | 18                     | 0.47      | 0.09      |
| 5     |        | L-tryptophan| 3                  | 0.26      | 0.05      |
|       |          |          | 18                     | 0.30      | 0.06      |
| 6     |        | L-cysteine| 3                      | 0.54      | 0.11      |
|       |          |          | 18                     | 0.61      | 0.12      |
| 7     |        | L-glutamic acid[c] | 2             | 0.44      | 0.09      |
|       |          |          | 18                     | 0.45      | 0.09      |
| 8     |        | L-glutamine[c] | 2                  | 0.24      | 0.05      |
|       |          |          | 18                     | 0.26      | 0.05      |
| 9     |        | L-histidine[c] | 3                  | 0.41      | 0.08      |
|       |          |          | 18                     | 0.72      | 0.14      |
| 10    |        | L-serine[c] | 3                  | 0.38      | 0.08      |
|       |          |          | 18                     | 0.54      | 0.11      |
| 11    |        | L-threonine[c] | 2                  | 0.46      | 0.09      |
|       |          |          | 18                     | 0.49      | 0.10      |
| 12    |        | L-lysine[c] | 3                  | 3.05      | 0.61      |
|       |          |          | 18                     | 3.63      | 0.73      |
| 13    | None    |          | 2                      | n.d.      | -         |
|       |          |          | 18                     | n.d.      | -         |

Conditions: AA (5.0 mmol), H₂O (1.0 mL), CO₂ (2 bar), stirred at r.t. [a] Calculated by gravimetric analysis [b] mols of CO₂ captured per mol of AA. [c] AAs involved as RuBisCO active site. n.d.= not detectable. Experiments were performed at least twice; average values are used (St. Dev.<10%).
Capture with CO\textsubscript{2} (20 bar): L-lysine (5.0 mmol) was added in a 50 mL autoclave equipped with a magnetic stir bar, followed with 1.0 mL of DI water, then 20 bar of CO\textsubscript{2} was charged into the 50 mL autoclave. Afterwards, the autoclave was closed and stirred at r.t. for 0.5-3 h. The captured CO\textsubscript{2} amounts were calculated by $^{13}$C NMR-quant with THF (406.2 μL, 5.0 mmol) as internal standard.\textsuperscript{3}

Capture from ambient air: L-lysine (5.0 mmol) was added in a 25 mL vial followed with 15.0 mL of DI water, then the indoor air (containing ca. 400 ppm CO\textsubscript{2}) was bubbled through the vial using a long needle (1 L/min.). After 4 days, the amount of the solvent reduced to ca. 1 mL due to the water evaporation. THF (406.2 μL, 5.0 mmol) was added as an internal standard to the solution, and the mixture was analyzed by $^{13}$C NMR-quant.\textsuperscript{3}

| L-lysine (5.0 mmol scale) | Before air bubbling (1 mL solution) | Before air bubbling (15 mL solution) | After air bubbling 4 days (1 mL solution) |
|---------------------------|-----------------------------------|-----------------------------------|---------------------------------------|
| L-lysine (20.0 mmol scale) | Before air bubbling (5 mL solution) | Before air bubbling (15 mL solution) | After air bubbling 4 days (5 mL solution) |

Figure S1. Typical reaction mixture of CO\textsubscript{2} capture from ambient air with L-lysine.
Figure S2. $^{13}$C NMR-quant (185 - 150 ppm) in D$_2$O of a) L-lysine and corresponding solution after CO$_2$ capture with b) 20 bars of CO$_2$ (3 h), c) 2 bars of CO$_2$ (18 h) and d) air bubbling (1 L/min.) 4 d.

Figure S3. $^{13}$C NMR-quant (190 - 0 ppm) in D$_2$O of a) L-lysine and corresponding solution after CO$_2$ capture with b) 20 bars of CO$_2$ (3 h), c) 2 bars of CO$_2$ (18 h) and d) air bubbling (1 L/min.) 4 d.
Figure S4. $^{13}$C NMR-quant of L-lysine in D$_2$O.

Figure S5. $^{13}$C NMR-quant in D$_2$O of CO$_2$ capture under 20 bars of CO$_2$ (3 h) with 5.0 mmol L-lysine.
Figure S6. $^{13}$C NMR-quant in D$_2$O of CO$_2$ capture under 2 bars of CO$_2$ (18 h) with 5.0 mmol L-lysine.

Figure S7. $^{13}$C NMR-quant in D$_2$O of CO$_2$ capture with air bubbling (1 L/min. 1 day) with 5.0 mmol L-lysine.
Figure S8. $^{13}$C NMR-quant in D$_2$O of CO$_2$ capture with air bubbling (1 L/min. 2 days) with 5.0 mmol L-lysine.

Figure S9. $^{13}$C NMR-quant in D$_2$O of CO$_2$ capture with air bubbling (1 L/min. 4 days) with 5.0 mmol L-lysine.
Figure S10. $^{13}$C NMR-quant in D$_2$O of CO$_2$ capture with air bubbling (1 L/min. 8 days) with 5.0 mmol L-lysin.

Figure S11. $^{13}$C NMR-quant in D$_2$O of CO$_2$ capture with air bubbling (1 L/min. 4 days) with 20.0 mmol L-lysin.
Standard procedure for the hydrogenation of gaseous CO$_2$

Given amount of catalyst dosed from a stock solution (1 mg catalyst dissolved in 10 mL THF), amino acid (5.0 mmol) and solvent (10 mL) were added to a 50 mL autoclave equipped with a magnetic stir bar. After pressurizing the reactor with CO$_2$ gas, the reaction mixture was stirred at r.t. for 30 min. The reactor was pressurized with H$_2$ gas then heated and stirred on a pre-heated oil bath for indicated time. The reactor was cooled to r.t. and a biphasic reaction mixture containing a transparent upper layer and a yellow lower layer was obtained. DI water (ca. 3 mL) was added to the above mixture resulting in a homogeneous solution. DMF (250 μL, 3.24 mmol) was added as an internal standard to the reaction mixture. The reaction mixture was then analyzed by $^1$H NMR with a few drops of D$_2$O (ca. 2 mL) to lock the signals.$^4$

| 5.0 mmol L-lysine | Before reaction (two-phase) | After reaction (two-phase) | After reaction (3 mL DI water added) |
|-------------------|-----------------------------|---------------------------|-------------------------------------|
| 20.0 mmol L-lysine| Before reaction (two-phase) | After reaction (two-phase) | After reaction (10 mL DI water added) |

*Figure S12. Typical reaction mixture of the hydrogenation of CO$_2$ to formate in the presence of L-lysine.*
Figure S13. Typical $^1$H NMR in D$_2$O after hydrogenation of gaseous CO$_2$ to formate in the presence of L-lysine.
Table S2. Hydrogenation of CO₂ in the presence of various amino acids.

| Entry | AAs                      | Formate [mmol][a] | Yield [%][b] | Formate [TON][c] |
|-------|--------------------------|-------------------|-------------|------------------|
| 1     | L-lysine[d]              | 0.71              | 71          | 355              |
| 2     | glycine                  | n.d.              | -           | -                |
| 3     | L-proline                | n.d.              | -           | -                |
| 4     | L-methionine             | n.d.              | -           | -                |
| 5     | L-tyrosine               | n.d.              | -           | -                |
| 6     | L-tryptophan             | n.d.              | -           | -                |
| 7     | L-cysteine               | 0.04              | 4           | 20               |
| 8     | L-glutamic acid[d]       | n.d.              | -           | -                |
| 9     | L-glutamine[d]           | n.d.              | -           | -                |
| 10    | L-histidine[d]           | 0.125             | 13          | 63               |
| 11    | L-serine[d]              | 0.1               | 10          | 50               |
| 12    | L-threonine[d]           | 0.045             | 5           | 23               |

Conditions: AA (1.0 mmol), Ru-MACHO-BH (2.0 μmol, 0.2 mol%), H₂O (1.0 mL), THF (1.0 mL), CO₂ (20 bar), H₂ (60 bar), 145 °C, 40 h. [a] Determined by ¹H NMR with DMF (38.5 μL, 0.5 mmol) as internal standard. [b] Calculated by formate [mmol]/AA [mmol]. [c] Calculated by formate [mmol]/catalyst [mmol]. [d] AAs involved as RuBisCO active site. n.d. = not detectable. Experiments were performed at least twice; average values are used (St. Dev.<10%).
Table S3. Hydrogenation of CO$_2$ with L-lysine (blank reactions).

![Chemical structure](Ru-1_Ru-MACHO-BH)

\[
\text{CO}_2 + \text{H}_2 + \text{Lys} \rightarrow \text{[LysH]}^+[\text{HCOO}]^-
\]

| Entry | L-lysine [mmol] | Cat. [μmol, ppm] | Formate [mmol][a] | Yield [%][b] |
|-------|----------------|------------------|-------------------|-------------|
| 1     | 5              | 2.0, 400 ppm     | 4.37              | 87          |
| 2     | None           | 2.0, 400 ppm     | n.d.              | -           |
| 3     | 5              | None             | n.d.              | -           |
| 4     | 5              | 2.0, 400 ppm     | n.d.              | -           |

Conditions: L-lysine (5.0 mmol), Ru-MACHO-BH (2.0 μmol, 400 ppm), H$_2$O (5.0 mL), THF (5.0 mL), CO$_2$ (20 bar), H$_2$ (60 bar), 145 °C, 12 h. [a] Determined by $^1$H NMR with DMF (250 μL, 3.24 mmol) as internal standard. [b] Calculated by formate [mmol]/L-lysine [mmol]. [c] In the absence of CO$_2$. n.d. = not detectable.

Table S4. Hydrogenation of CO$_2$ with L-lysine (screening of solvents).

![Chemical structure](Ru-1_Ru-MACHO-BH)

\[
\text{CO}_2 + \text{H}_2 + \text{Lys} \rightarrow \text{[LysH]}^+[\text{HCOO}]^-
\]

| Entry | Solvent [mL] | Formate [mmol][a] | Yield [%][b] | Formate [TON][c] |
|-------|--------------|-------------------|-------------|-----------------|
| 1     | THF [5] + H$_2$O [5] | 4.37              | 87          | 2,187           |
| 2     | 2-MTHF [5] + H$_2$O [5] | 4.30              | 86          | 2,148           |
| 3     | Triglyme [5] + H$_2$O [5] | 3.27              | 65          | 1,636           |
| 4     | MeOH [5] + H$_2$O [5] | 3.18              | 64          | 1,588           |
| 5     | Ethylene glycol [5] + H$_2$O [5] | 1.23              | 25          | 617             |
| 6     | THF [10]  | 0.62              | 12          | 308             |
| 7     | 2-MTHF [10] | 0.35              | 7           | 177             |
| 8     | Triglyme [10] | 0.55              | 11          | 275             |
| 9     | MeOH [10] | 0.52              | 10          | 259             |
| 10    | Ethylene glycol [10] | 1.13              | 23          | 567             |
| 11    | H$_2$O [10] | 0.49              | 9           | 243             |

Conditions: L-lysine (5.0 mmol), Ru-MACHO-BH (2.0 μmol, 400 ppm), solvent (10.0 mL in total), CO$_2$ (20 bar), H$_2$ (60 bar), 145 °C, 12 h. [a] Determined by $^1$H NMR with DMF (250 μL, 3.24 mmol) as internal standard. [b] Calculated by formate [mmol]/L-lysine [mmol]. [c] Calculated by formate [mmol]/catalyst [mmol]. Experiments were performed at least twice; average values are used (St. Dev.<10%)
Table S5. Hydrogenation of CO₂ with L-lysine (screening of temperature and time).

\[
\text{CO}_2 + \text{H}_2 + \text{Lys} \xrightarrow{\text{Ru-1 (0.02 \mu mol, 4 ppm)}} \frac{\text{H}_2\text{O} (5.0 \text{ mL}), \text{THF} (5.0 \text{ mL})}{[\text{LysH}][\text{HCOO}^-]} 
\]

| Entry | T [°C] | Time [h] | Formate [mmol][a] | Yield [%][b] | Formate [TON][c] |
|-------|--------|----------|-------------------|-------------|-----------------|
| 1     | 145    | 12       | 3.95              | 79          | 197,559         |
| 2     | 145    | 3        | 2.77              | 55          | 138,510         |
| 3     | 105    | 12       | 3.22              | 64          | 161,028         |

Conditions: L-lysine (5.0 mmol), Ru-MACHO-BH dosed from stock solution (0.02 \mu mol, 4 ppm), H₂O (5.0 mL), THF (5.0 mL), CO₂ (20 bar), H₂ (60 bar). [a] Determined by 1H NMR with DMF (250 \mu L, 3.24 mmol) as internal standard. [b] Calculated by formate [mmol]/L-lysine [mmol]. [c] Calculated by formate [mmol]/catalyst [mmol]. Experiments were performed at least twice; average values are used (St. Dev.<10%).

Table S6. Conditions for the generation of formamides from formates.

\[
\text{RNH}_2 + \text{HOOH} \xrightarrow{\text{r.t., 0.5 h}} \frac{\text{HOO}}{\text{R-NH}_3} \xrightarrow{\text{145 °C, 12 h}} \frac{\text{HNHR}}{\text{H}_2\text{O}} 
\]

| Entry | Amine [5 mmol] | Formates [%yield][a] | Formamides [%yield][a] | pH of free amine |
|-------|----------------|----------------------|------------------------|------------------|
| 1     | L-lysine       | >99                  | n.d.                   | 10.2             |
| 2     | PEHA           | 71                   | 28                     | 13.4             |

Conditions: Formic acid (5 mmol), L-lysine (5 mmol) or PEHA (5 mmol), H₂O (5 mL) as solvent, stirred at 145 °C, 12 h. pH of free amine was measured with 5 M concentration in H₂O at 25 °C. [a] Determined by ¹H NMR with DMF (250 \mu L, 3.24 mmol) as internal standard. n.d. = not detectable.
Standard procedure for CO$_2$ capture from ambient air and *in situ* conversion to formate.

The total volume of the solution of CO$_2$ capture from indoor air reduced to ca. 1 mL due to water evaporation. This mixture was firstly bubbled with argon for 30 min. then transferred using 4 mL of degassed DI water to a 50 mL autoclave equipped with a magnetic stir bar. The given amounts of catalyst (dosed from stock solution in THF) and THF (5 mL) were added to the above mixture. After pressurizing the reactor with H$_2$, the reaction mixture was stirred and heated on a pre-heated oil bath for indicated time. The reactor was cooled to r.t. and a biphasic reaction mixture containing a transparent upper layer and a pale yellow lower layer was obtained. DI water (ca. 3 mL) was added to the above mixture resulting in a homogeneous solution. DMF (250 μL, 3.24 mmol) was added as an internal standard to the reaction mixture. The reaction mixture was then analyzed by $^1$H NMR with a few drops of D$_2$O (ca. 2 mL) to lock the signals. 

| 5.0 mmol L-lysine | After reaction (two-phase) | After reaction (3 mL DI water added) |
|-------------------|---------------------------|-------------------------------------|
| Before reaction (two-phase) | After reaction (two-phase) | After reaction (3 mL DI water added) |

| 20.0 mmol L-lysine | After reaction (two-phase) | After reaction (10 mL DI water added) |
|-------------------|---------------------------|-------------------------------------|
| Before reaction (two-phase) | After reaction (two-phase) | After reaction (10 mL DI water added) |
**Figure S14.** Typical reaction mixture for the hydrogenation of captured CO$_2$ to formate.

**Figure S15** Typical $^1$H NMR in D$_2$O after hydrogenation of captured CO$_2$ to formate.

**Figure S16.** Typical $^{13}$C NMR in D$_2$O after hydrogenation of captured CO$_2$ to formate.
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