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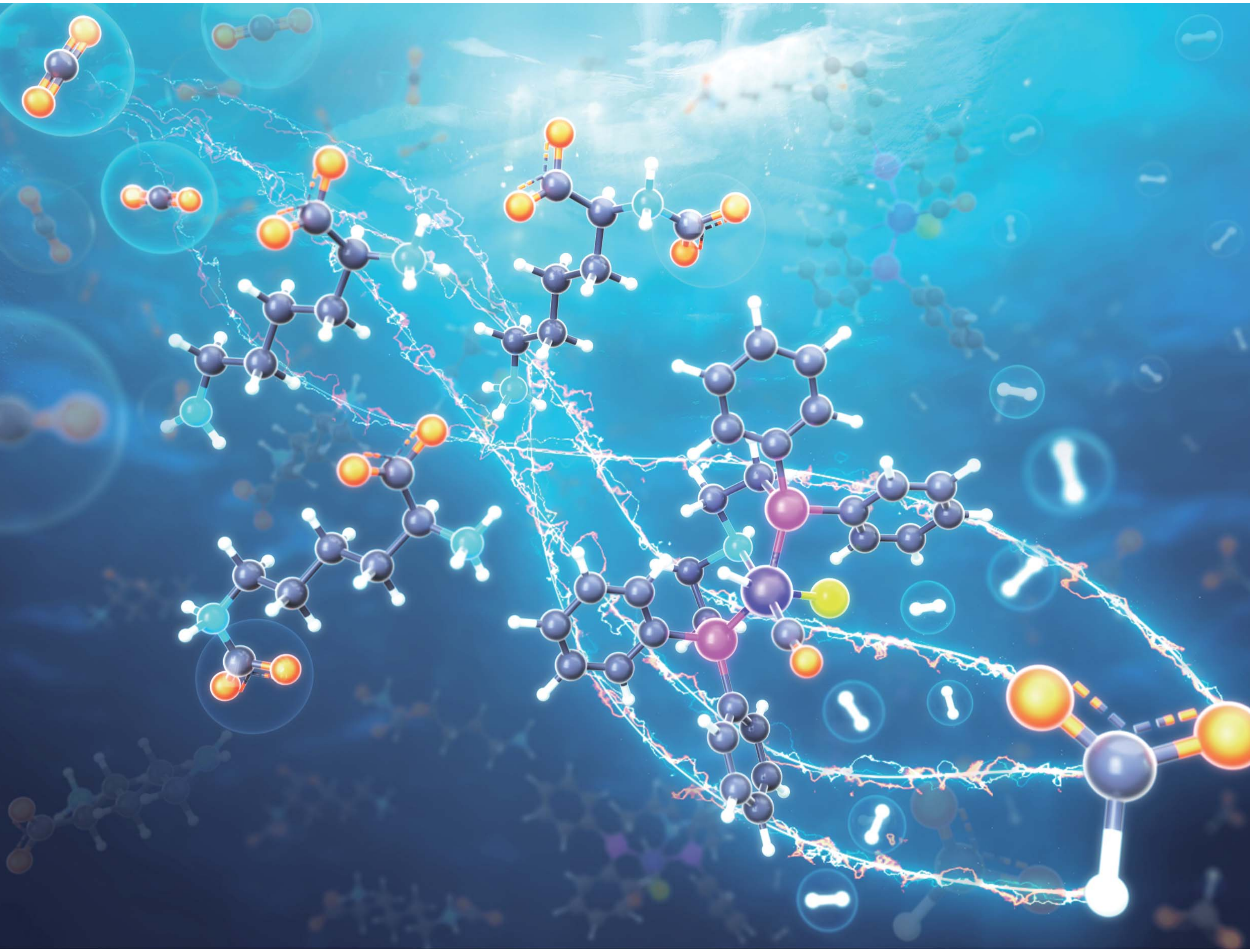

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An amino acid based system for CO_2 capture and catalytic utilization to produce formates†

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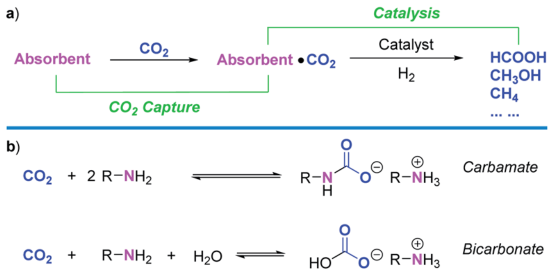
Herein, we report a novel amino acid based reaction system for CO_2 capture and utilization (CCU) to produce formates in the presence of the naturally occurring amino acid L-lysine. Utilizing a specific ruthenium-based catalyst system, hydrogenation of absorbed carbon dioxide occurs with high activity and excellent productivity. Noteworthy, following the CCU concept, CO_2 can be captured from ambient air in the form of carbamates and converted directly to formates in one-pot (TON > 50 000). This protocol opens new potential for transforming captured CO_2 from ambient air to C1-related products.

Introduction

Carbon dioxide concentration in the atmosphere and global warming is ever-increasing with the enormous global energy demand supplied by consuming fossil fuels (mainly coal, oil, and natural gas).[1,2] CO_2 capture and storage (CCS) enable the use of fossil fuels with significantly lower CO_2 emissions than usual.[3] CCS is based on the separation of CO_2 from energy conversion or other industrial processes, followed by compression, transport, and storage. However, CCS processes are meanwhile energy intensive as the electricity burden with amine scrubbing (113 kW h per mt CO_2 removed) constitutes the minimum work to separate and compress CO_2 (150 bar). Indeed, in two demonstration units, Boundary Dam and Thompsons, 210–220 kW h per mt were required for this purpose.[4] Developing novel CO_2 capture and utilization (CCU) methods for converting CO_2 from air or flue gas not only saves energy from CCS (mainly CO_2 desorption and compression steps) but also provides C1-related products (Scheme 1a).[5–12] It's thus an important opportunity for developing a sustainable economy.[13–15]

In nature, inorganic carbon (particularly CO_2) is converted to organic compounds by living organisms, which is known as carbon fixation, with photosynthesis as the most prominent example.[16] It is estimated that approximately 258 billion tons of CO_2 are converted into biomass by photosynthesis annually.[17] As the most abundant protein on the Earth, ribulose 1,5-bisphosphate carboxylase/oxygenase (RuBisCO) is involved in the first major step of carbon fixation by plants and other photosynthetic organisms.[18,19] L-Lysine (Lys) is one of the six crucial amino acids (AAs) that are part of the active site of RuBisCO and it stabilizes CO_2 in the form of carbamate for subsequent enzyme catalysis.[20]

By contrast, in industry *e.g.*, power plants, the most common process for capturing CO_2 relies on the use of aqueous amine solutions (Scheme 1b).[3,21,22] However, the maximum CO_2 absorption capacity for an amine system varies based on which products are formed. When carbamates are the preferred products, this capacity is 50 mol% per amines at most. If bicarbonates are mainly formed, this capacity could reach up to 100 mol% per amines. Alkanolamines have been extensively investigated as chemical absorbents;[23] however, their large-scale use also created some environmental concerns. Substituting such conventional amine absorbents with high boiling and innocuous natural AAs in combining CO_2 capture and catalysis is therefore highly relevant. Noteworthy, CO_2 capture with aqueous AAs,[24–27] including Lys[25] was already reported, but not its direct valorization. Based on the infusive phenomenon of carbon fixation by RuBisCO and our long-term interest in CO_2 reduction, we report herein a CCU process which enables CO_2 capture from ambient air and its conversion to formate in the presence of L-lysine. Moreover, to the best of our knowledge, there exists no example of catalytic hydrogenation of CO_2 assisted by AAs.



Scheme 1 (a) Schematic CCU concept for CO_2 hydrogenation to C1 products. (b) Reaction pathways for CO_2 absorption with amines under aqueous conditions.

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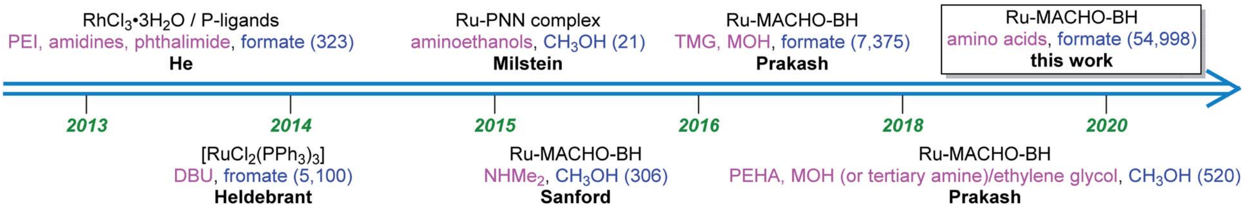


Fig. 1 Representative catalysts and absorbents for CO_2 hydrogenation to C1 products applied in CCU processes. The highest TON (turnover number) of formates or methanol are shown in parentheses, respectively.

Several Rh- and Ru-based homogeneous catalysts have been previously reported for CO_2 capture and *in situ* hydrogenation to C1 products (Fig. 1).[8,28] In 2013, pioneering work was performed by the group of He utilizing $RhCl_3 \cdot 3H_2O$ and phosphine ligands, for instance $CyPPh_2$, DPEphos, and PPh_3, as catalysts where gaseous CO_2 was absorbed by polyethyleneimine (PEI),[29] amidines,[30] and potassium phthalimide[31] as well as hydrogenated *in situ* to formates or formic acid.

In addition, ruthenium complexes have also been proven to be suitable catalysts for the hydrogenation of captured CO_2 to formate or methanol. In 2014, Heldebrant and co-workers captured CO_2 by DBU in methanol to form the methyl carbonate, which then was hydrogenated to formates catalyzed by $[RuCl_2(PPh_3)_3]$.[32] One year later, Milstein and co-workers reported a CCU approach, where CO_2 reacted with aminoethanols yielding oxazolidinones which were hydrogenated to CH_3OH in 78–92% yield with a Ru-PNN pincer catalyst.[33] In the same year, the Sanford group reported the CO_2 capture with $NHMe_2$ to form carbamate and subsequent hydrogenation to a mixture of DMF and CH_3OH catalyzed by Ru-MACHO-BH complex.[34] Employing the same catalyst and tetramethylguanidine (TMG),[35] metal hydroxides,[36] pentaethylenehexamine (PEHA),[37–39] a mixture of metal hydroxides,[40] or a tertiary amine[41] with ethylene glycol as CO_2 absorbent systems, Prakash and his colleagues combined CO_2 capture from air with subsequent hydrogenation to produce formates or methanol. Recently, the group of Heldebrant reported a method where epoxides reacted with CO_2 leading to cyclic carbonates. Then, *in situ* hydrogenation took place into methanol and glycol, with Ru-MACHO as catalyst.[42]

Compared to methanol, no hydrogen is lost in the form of water when formic acid or formate salts are produced by CO_2 hydrogenation. Currently, formic acid is industrially produced by carbonylation of methanol to methyl formate and subsequent hydrolysis.[43] It is mainly used as a preservative and antibacterial agent in livestock feed, *e.g.* silage and winter feed for cattle. In addition, formic acid is utilized in the production of leather and in dyeing and finishing textiles. More recently, it also gained interest as hydrogen storage medium as it contains 4.4 wt% of hydrogen with 53 g H_2 per L of volumetric storage density.[7]

Results and discussion

CO_2 capture with amino acids

For the development of a CCU concept to produce formic acid or formates, suitable CO_2 absorbents must be used. Inspired by the carbon fixation pattern in nature, specifically RuBisCO, we considered applying AAs for this purpose.[24–27] Thus, at the start of our investigations, we evaluated the ability of 12 different AAs, including the 6 ones involved in the active site of RuBisCo and some analogues to capture CO_2. For this purpose, CO_2 (2 bar) was charged into an aqueous solution of the respective AAs (5 M) and stirred at r.t. for 2–18 h.

As shown in Table S1,† most of the tested systems such as L-proline, L-glutamine, and L-histidine achieved only small to moderate amounts of CO_2 capture, around 0.1 mol of CO_2 per mol of AA (CO_2/AA), (Table S1, entries 1–11†). Interestingly, in the presence of L-lysine (Lys), a significantly improved performance (3.63 mmol of captured CO_2, corresponding to 0.73 CO_2/Lys) was obtained in 18 h (Table S1, entry 12†). Such high CO_2 capture efficiency could be attributed to the basic side chain of Lys, as its pK_a value is 10.7.

Thus, we investigated the effect of Lys for CO_2 absorption under various conditions (Table 1 and Fig. S2 to S11†). As mentioned *vide supra*, carbon dioxide can be captured in form of Lys carbamates[26] or Lys ammonium bicarbonate.[44] Applying 20 bar of CO_2, 0.83 CO_2/Lys were obtained within only 0.5 h leading to carbamates and bicarbonate (ratio of 1 : 4, 98% total yield; Table 1, entry 1). A similar result was observed after 3 h (Table 1, entry 2). Also, at lower CO_2 pressure (2 bar), significant absorption was achieved with 69–98% total yield of carbamates and bicarbonate within 0.5–18 h (Table 1, entries 3–5). Interestingly, in these cases (0.5 h and 3 h), mainly Lys carbamates were obtained. This shows that initially the corresponding carbamates are formed, which subsequently form bicarbonate.

Besides water, the aprotic solvent THF was applied. After 3 h exclusively the carbamate was formed (1.18 mmol corresponding to 0.24 CO_2/Lys, Table 1, entry 6). A much lower CO_2/Lys ratio (0.06) was observed under neat conditions (without solvent, Table 1, entry 7). Next, to demonstrate the viability of our general CCU methodology, ambient air, containing *ca.* 415 ppm (parts per million) CO_2, was bubbled through Lys solution for 1–8 days (Fig. S1†). Indeed, up to 0.49 mol CO_2 per mol Lys were absorbed representing a yield of 98% with carbamates as sole products. Performing the reaction on multi-g scale (20 mmol Lys), 8.20 mmol CO_2 were captured corresponding to 0.41 CO_2/Lys and 82% carbamate yield (Table 1, entry 12).

Catalytic hydrogenation of CO_2 to formate

Next, to identify a suitable reduction system, various metal pincer complexes were tested for the hydrogenation of gaseous CO_2 in the presence of different amino acids (Tables 2 and S2,

Table 1 CO_2 capture with Lys according to Scheme 1b under various conditions[a]

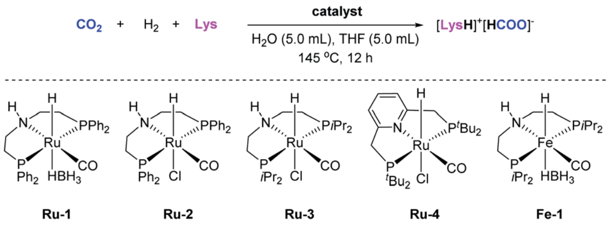
Entry	CO_2 source	Time	Carbamates[b] [mmol]	Bicarbonate[b] [mmol]	Yield[c] [%]	CO_2/Lys[d]
1	CO_2 (20 bar)	0.5 h	0.75	3.40	98%	0.83
2	CO_2 (20 bar)	3 h	0.45	3.80	94%	0.85
3	CO_2 (2 bar)	0.5 h	1.53	0.37	69%	0.38
4	CO_2 (2 bar)	3 h	1.83	1.22	98%	0.61
5	CO_2 (2 bar)	18 h	1.25	2.38	98%	0.73
6[e]	CO_2 (2 bar)	3 h	1.18	n.d.	47%	0.24
7[f]	CO_2 (2 bar)	3 h	0.30	n.d.	12%	0.06
8	Air	1 d	1.40	n.d.	56%	0.28
9	Air	2 d	1.95	n.d.	78%	0.39
10	Air	4 d	2.42	n.d.	97%	0.48
11	Air	8 d	2.45	n.d.	98%	0.49
12[g]	Air	4 d	8.20	n.d.	82%	0.41

[a] Conditions: Lys (5.0 mmol), H_2O (1.0 mL), stirred at r.t. Air bubbling: 1 L min^{-1}. [b] Determined by ^{13}C NMR-quant with THF (406.2 μL, 5.0 mmol) as internal standard. [c] Total yield of carbamates and bicarbonate based on Lys. [d] Mols of CO_2 captured per mol of Lys. [e] THF (1 mL) as solvent. [f] Neat condition (without solvent). [g] Lys 20.0 mmol. n.d. = not detectable. Experiments were performed at least twice; average values are used (st. dev. < 10%).

Fig. S12 and S13†). To our delight, testing the Ru-MACHO-BH complex (**Ru-1**, 0.2 mol%) in H_2O/THF (1 : 1 mixture) revealed significant activity in the presence of Lys for the hydrogenation of gaseous CO_2 to formate (71% yield based on Lys) at 145 °C (Table S2, entry 1†).

On the other hand, L-cysteine, L-histidine, L-serine, and L-threonine led to formates in much lower yields (up to 13%), while other AAs, such as glycine, L-proline, and L-glutamine showed no activity at all in the presence of catalyst **Ru-1**, (Table S2, entries 2–12†). Taking Lys as a benchmark CO_2 absorbent, the TON of formate can be considerably increased from 2187 to 197 559 when decreasing the loading of **Ru-1** from 400 ppm (based on Lys) to 4 ppm (Table 2, entries 1–3). With 4 ppm of Ru-MACHO (**Ru-2**) as catalyst, the highest TON 212 139 was achieved (Table 2, entry 4). Interestingly, in these reactions, CO_2 was selectively converted to formate in up to 87% yield with less than 1% of formamide. Next, several ruthenium pincer complexes were tested at 4 ppm loading for the hydrogenation of gaseous CO_2 in the presence of Lys within 3 h (Table 2, entries 6–10). **Ru-1** and **Ru-2** gave formate in 55% and 58% yields, respectively, whereas Ru-MACHO^{iPr} (**Ru-3**) was less active leading to formate in only 6% yield. With Milstein's Ru-PNP complex (**Ru-4**) as catalyst, formate was obtained in 47% yield. However, no formate can be detected in the reaction catalyzed by Fe-MACHO^{iPr}-BH complex (**Fe-1**).

Table 2 Ru-catalyzed hydrogenation of gaseous CO_2 in the presence of Lys[a]



Entry	Cat. [μmol, ppm]	Formate[b] [mmol]	% Yield[c] (TON)[d]
1	**Ru-1** [2.0, 400]	4.37	87 (2187)
2	**Ru-1** [0.2, 40]	3.89	78 (19 440)
3	**Ru-1** [0.02, 4]	3.95	79 (197 559)
4	**Ru-2** [0.02, 4]	4.24	85 (212 139)
5	**Ru-2** [0.01, 2]	1.48	30 (147 906)
6[e]	**Ru-1** [0.02, 4]	2.77	55 (138 510)
7[e]	**Ru-2** [0.02, 4]	2.90	58 (144 990)
8[e]	**Ru-3** [0.02, 4]	0.29	6 (14 580)
9[e]	**Ru-4** [0.02, 4]	2.35	47 (117 450)
10[e]	**Fe-1** [0.02, 4]	n.d.	—

[a] Conditions: catalyst, Lys (5.0 mmol), H_2O (5.0 mL), THF (5.0 mL), CO_2 (20 bar), H_2 (60 bar), 145 °C, 12 h. [b] Determined by ^1H NMR with DMF (250 μL, 3.24 mmol) as internal standard. [c] Calculated by formate [mmol]/Lys [mmol]. [d] Calculated by formate [mmol]/catalyst [mmol]. [e] 3 h. n.d. = not detectable. Experiments were performed at least twice; average values are used (st. dev. < 10%).

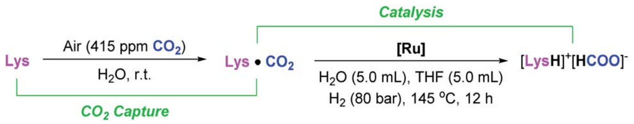
Several blank reactions were also carried out (Table S3†): in the absence of either Lys, **Ru-1**, or CO_2, no formate was detectable. These results clearly demonstrate that Lys and **Ru-1** are both crucial to promote the hydrogenation of CO_2 from air to formate. Reactions with other solvents, for example, triglyme, methanol, ethylene glycol or their 1 : 1 mixture with water could not improve the reaction efficiency (Table S4†). When replacing THF with the more eco-friendly green solvent 2-methyltetrahydrofuran (2-MTHF),[45] a comparable yield of formate (86%) was observed. Lowering the temperature from 145 to 105 °C, the yield of formate decreased only slightly from 79% to 64% (Table S5†).

Development of a general CCU concept

After having studied the individual processes of (a) CO_2 absorption and (b) CO_2 reduction in the presence of Lys, the overall CCU concept was demonstrated by combining CO_2 capture and *in situ* hydrogenation to formate (Table 3 and Fig. S14–S16†).

Using captured CO_2 (2.42 mmol) as substrate in the presence of **Ru-1** (2.0 μmol) as catalyst, 46% formate yield (based on

Table 3 Combining CO_2 capture from ambient air and *in situ* conversion to formate[a]



Entry	Captured CO_2 [mmol]	Cat. [μmol]	Formate[b] [mmol]	% Yield[c] (TON)[d]
1	2.42	**Ru-1** [2.0]	1.10	46 (551)
2	2.42	**Ru-1** [0.85]	1.15	48 (1353)
3	2.42	**Ru-1** [0.17]	1.02	42 (6004)
4	2.42	**Ru-1** [0.02]	1.10	45 (54 998)
5	2.42	**Ru-2** [0.02]	1.04	43 (52 245)
6[e]	8.20	**Ru-1** [0.08]	2.40	29 (29 993)
7[e]	8.20	**Ru-2** [0.08]	3.31	40 (41 330)
8[e]	8.20	**Ru-2** [0.04]	1.00	12 (25 110)

[a] Conditions: CO_2 captured from air within 4 d applying 5 mmol Lys, given amount of catalyst dosed from stock solution, H_2O (5.0 mL), THF (5.0 mL), H_2 (80 bar), 145 °C, 12 h. [b] Determined by ^1H NMR with DMF (250 μL, 3.24 mmol) as internal standard. [c] Calculated by formate [mmol]/captured CO_2 [mmol]. [d] Calculated by formate [mmol]/catalyst [mmol]. [e] CO_2 captured with 20 mmol Lys. Experiments were performed at least twice; average values are used (st. dev. < 10%).

captured CO_2) was obtained (TON 551; Table 3, entry 1). The highest TON reached 54 998 with 0.02 μmol **Ru-1**, while the yield was maintained at 45% (Table 3, entries 2–4). **Ru-2** showed comparable activity for the hydrogenation of captured CO_2 yielding 43% of formate (Table 3, entry 5). With 8.20 mmol captured CO_2, 29% of formate were obtained with **Ru-1** at 0.08 μmol loading (Table 3, entry 6). 3.31 mmol formate (40% yield) were obtained with the same amount of **Ru-2** (Table 3, entry 7).

Finally, some Lys analogues and derivatives as well as selected benchmark amines[35,37,39] were applied according to our overall protocol (Fig. 2). In the presence of 6-aminohexanoic acid and 1,5-diaminopentane, 0.12 and 0.82 CO_2/amine were achieved and formates were obtained in yields of 25% and 34%, respectively. Noticeably, 2,3-diaminopropanoic acid and the simplest amino acid glycine did not show any activity in both CO_2 absorption and hydrogenation processes. In the case of TMG and PEHA, CO_2 was captured with 0.86 and 0.83 CO_2/TMG or PEHA, respectively. However, the presence of TMG inhibited the hydrogenation of CO_2, whereas PEHA led to formate and formamides in 38% and 8% yield, respectively. Applying the inorganic base NaOH[36] resulted in a CO_2/base ratio of 1.08 and 23% formate yield. All these experiments demonstrate the superiority of using Lys for carbon dioxide capture and direct valorizations. It also indicates the crucial presence of an α-amino acid moiety and an additional amine function in the side chain of AA.

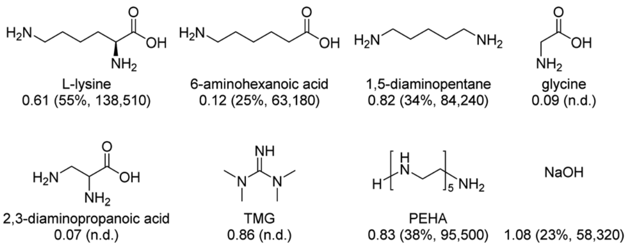


Fig. 2 Various Lys analogues and benchmark amines applied in the CO_2 absorption and hydrogenation processes performed under conditions in Table 1, entry 4 and Table 2 entry 6, respectively. CO_2/amine (mols of CO_2 captured per mol of amine) are shown with yield and TON of formates in parentheses; n.d. = not detectable.

To rationalize the perfect selectivity towards formates in the current study, we conducted further experiments by heating up the mixture of formic acid and Lys or PEHA in H_2O at 145 °C (Table S6†). Indeed, Lys led to formate in quantitative yield without any formamide detectable after 12 h, whereas PEHA gave 28% yield of formamide along with 71% formate. Obviously, the less basic conditions applying Lys (pH 10.2 for a 5 M aqueous solution) prevented the formation of formamides taking place in the presence of PEHA (pH 13.4).

Conclusions

In conclusion, we described an amino acid based catalyst system for the highly relevant CO_2 capture and utilization (CCU) process to produce formates in one-pot. The naturally occurring amino acid L-lysine affords formate generation with a high efficiency. Among the investigated catalysts, the most active ones are identified with Ru-MACHO complexes (**Ru-1** and **Ru-2**) for the hydrogenation of gaseous CO_2 (TON > 210 000) and the *in situ* hydrogenation of captured CO_2 (TON > 50 000). Noteworthy, in the present CCU concept, CO_2 can be captured from ambient air in the form of carbamates and hydrogenated to formate directly.

Author contributions

D. W. conducted all the experimental work, collected and analyzed the data. D. W., H. J. and M. B. wrote the paper. H. J. and M. B. proposed and supervised the project. All the authors discussed the results and commented on the manuscript. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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References

1 G. A. Olah, A. Goeppert and G. K. S. Prakash, *J. Org. Chem.*, 2009, **74**, 487–498.
2 W. Wang, S. Wang, X. Ma and J. Gong, *Chem. Soc. Rev.*, 2011, **40**, 3703–3727.
3 D. M. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem., Int. Ed.*, 2010, **49**, 6058–6082.
4 G. T. Rochelle, in *Absorption-Based Post-combustion Capture of Carbon Dioxide*, ed. P. H. M. Feron, Woodhead Publishing, 2016, pp. 35–67, DOI: 10.1016/B978-0-08-100514-9.00003-2.
5 M. Aresta, *Carbon dioxide as chemical feedstock*, Wiley-VCH, Weinheim, 2010.
6 T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365–2387.
7 K. Sordakis, C. Tang, L. K. Vogt, H. Junge, P. J. Dyson, M. Beller and G. Laurenczy, *Chem. Rev.*, 2018, **118**, 372–433.
8 S. Kar, A. Goeppert and G. K. S. Prakash, *Acc. Chem. Res.*, 2019, **52**, 2892–2903.
9 W.-H. Wang, X. Feng and M. Bao, *Transformation of Carbon Dioxide to Formic Acid and Methanol*, Springer, Singapore, 2018.
10 K. Dong, R. Razzaq, Y. Hu and K. Ding, *Top. Curr. Chem.*, 2017, **375**, 203–228.
11 Y. Li, Z. Wang and Q. Liu, *Chin. J. Org. Chem.*, 2017, **37**, 1978–1990.
12 W. H. Bernskoetter and N. Hazari, *Acc. Chem. Res.*, 2017, **50**, 1049–1058.
13 N. MacDowell, N. Florin, A. Buchard, J. Hallett, A. Galindo, G. Jackson, C. S. Adjiman, C. K. Williams, N. Shah and P. Fennell, *Energy Environ. Sci.*, 2010, **3**, 1645–1669.
14 A. Goeppert, M. Czaun, G. K. S. Prakash and G. A. Olah, *Energy Environ. Sci.*, 2012, **5**, 7833–7853.
15 E. S. Sanz-Pérez, C. R. Murdock, S. A. Didas and C. W. Jones, *Chem. Rev.*, 2016, **116**, 11840–11876.
16 A. Bar-Even, E. Noor, N. E. Lewis and R. Milo, *Proc. Natl. Acad. Sci. U. S. A.*, 2010, **107**, 8889–8894.
17 R. J. Geider, E. H. Delucia, P. G. Falkowski, A. C. Finzi, J. P. Grime, J. Grace, T. M. Kana, J. La Roche, S. P. Long and B. A. Osborne, *Glob. Change Biol.*, 2001, **7**, 849–882.
18 T. D. Sharkey, *Photosynth. Res.*, 2019, **140**, 235–252.
19 U. Feller, I. Anders and T. Mae, *J. Exp. Bot.*, 2008, **59**, 1615–1624.
20 B. Stec, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 18785–18790.
21 P. V. Kortunov, M. Siskin, L. S. Baugh and D. C. Calabro, *Energy Fuels*, 2015, **29**, 5919–5939.
22 F. Barzagli, F. Mani and M. Peruzzini, *Energy Environ. Sci.*, 2009, **2**, 322–330.
23 P. D. Vaidya and E. Y. Kenig, *Chem. Eng. Technol.*, 2007, **30**, 1467–1474.
24 A.-H. Liu, R. Ma, C. Song, Z.-Z. Yang, A. Yu, Y. Cai, L.-N. He, Y.-N. Zhao, B. Yu and Q.-W. Song, *Angew. Chem., Int. Ed.*, 2012, **51**, 11306–11310.
25 A.-A. Al-Terkawi, F. Lamaty and T.-X. Métro, *ACS Sustainable Chem. Eng.*, 2020, **8**, 13159–13166.
26 Y. Yamamoto, J. y. Hasegawa and Y. Ito, *J. Phys. Org. Chem.*, 2012, **25**, 239–247.
27 S. Shen, Y.-n. Yang, Y. Bian and Y. Zhao, *Environ. Sci. Technol.*, 2016, **50**, 2054–2063.
28 H.-C. Fu, F. You, H.-R. Li and L.-N. He, *Front. Chem.*, 2019, **7**, 1–15.
29 Y.-N. Li, L.-N. He, A.-H. Liu, X.-D. Lang, Z.-Z. Yang, B. Yu and C.-R. Luan, *Green Chem.*, 2013, **15**, 2825–2829.
30 Y.-N. Li, L.-N. He, X.-D. Lang, X.-F. Liu and S. Zhang, *RSC Adv.*, 2014, **4**, 49995–50002.
31 S. Zhang, Y. N. Li, Y. W. Zhang, L. N. He, B. Yu, Q. W. Song and X. D. Lang, *ChemSusChem*, 2014, **7**, 1484–1489.
32 M. Yadav, J. C. Linehan, A. J. Karkamkar, E. Van Der Eide and D. J. Heldebrant, *Inorg. Chem.*, 2014, **53**, 9849–9854.
33 J. R. Khusnutdinova, J. A. Garg and D. Milstein, *ACS Catal.*, 2015, **5**, 2416–2422.
34 N. M. Rezayee, C. A. Huff and M. S. Sanford, *J. Am. Chem. Soc.*, 2015, **137**, 1028–1031.
35 J. Kothandaraman, A. Goeppert, M. Czaun, G. A. Olah and G. K. S. Prakash, *Green Chem.*, 2016, **18**, 5831–5838.
36 S. Kar, A. Goeppert, V. Galvan, R. Chowdhury, J. Olah and G. K. S. Prakash, *J. Am. Chem. Soc.*, 2018, **140**, 16873–16876.
37 S. Kar, R. Sen, A. Goeppert and G. K. S. Prakash, *J. Am. Chem. Soc.*, 2018, **140**, 1580–1583.
38 J. Kothandaraman, A. Goeppert, M. Czaun, G. A. Olah and G. K. S. Prakash, *J. Am. Chem. Soc.*, 2016, **138**, 778–781.
39 S. Kar, R. Sen, J. Kothandaraman, A. Goeppert, R. Chowdhury, S. B. Munoz, R. Haiges and G. K. S. Prakash, *J. Am. Chem. Soc.*, 2019, **141**, 3160–3170.
40 R. Sen, A. Goeppert, S. Kar and G. K. S. Prakash, *J. Am. Chem. Soc.*, 2020, **142**, 4544–4549.
41 R. Sen, C. J. Koch, A. Goeppert and G. K. S. Prakash, *ChemSusChem*, 2020, **13**, 6318–6322.
42 J. Kothandaraman and D. J. Heldebrant, *RSC Adv.*, 2020, **10**, 42557–42563.
43 J. Hietala, A. Vuori, P. Johnsson, I. Pollari, W. Reutemann and H. Kieczka, in *Ullmann's Encyclopedia of Industrial Chemistry*, 2016, pp. 1–22, DOI: 10.1002/14356007.a12_013.pub3.
44 C. Perinu, B. Arstad and K.-J. Jens, *Energy Procedia*, 2013, **37**, 7310–7317.
45 A.-G. Sicaire, M. A. Vian, A. Filly, Y. Li, A. Bily and F. Chemat, in *Alternative Solvents for Natural Products Extraction*, Springer, 2014, pp. 253–268.