

Improved CO₂ Capture and Catalytic Hydrogenation Using Amino Acid Based Ionic Liquids

Ayeshe Moazezbarabadi⁺,^[a] Duo Wei⁺,^[a] Henrik Junge,^{*[a]} and Matthias Beller^{*[a]}

A series of alkyl ammonium (or imidazolium) based ionic liquids was tested as novel and potentially green absorbent for CO₂ capture and utilization. By exploiting various amino acids as counter ions for ionic liquids, CO₂ capture and hydrogenation to formate occur with high activity and excellent productivity

utilizing arginine. The reaction was easily scalable without any significant drop in formate production, and the catalyst was reused for five consecutive runs leading to an overall TON of 12,741 for the formation of formate salt.

Introduction


Carbon dioxide is one of the major contributors to greenhouse gas emissions and thereby responsible to a significant extent for climate change.^[1] Especially, burning fossil fuels, deforestation, and many other human activities resulted in a continuing increase of the concentration of CO₂ in the atmosphere in the past 150 years.^[2] Research shows that there is an undeniable link between global warming and the concentration of CO₂ (an important heat-trapping (greenhouse) gas) in the atmosphere.^[3] Therefore, the development of economic and cost-effective strategies for the reduction of CO₂ concentration in the atmosphere is of outmost importance for our societies. In principle, this goal can be achieved by implementing three different strategies: 1) reducing the amount of produced CO₂; 2) storing excess CO₂; and 3) using CO₂ as a C₁ source to produce fuels and other added-value chemicals utilizing renewable energy.^[4] The first strategy requires replacing carbon-rich fossil fuels such as coal, oil, and natural gas with sources having a reduced CO₂ footprint like biomass and affordable renewable energy.^[5] Storage and sequestration of CO₂ needs the development of new technologies for energy- and cost-efficient capture and storage of CO₂ underground in geological formations.^[6] The third strategy, utilization of CO₂ as an inexpensive, safe, and renewable C₁ building block to produce fuels and other value-added products is highly desired with respect to a circular carbon economy.^[7]


Currently, available CO₂ capture technologies are based mainly on amines, for example monoethanolamine (MEA).^[8] However, the reaction of CO₂ with amine-based solvents is energy intensive due to the large enthalpy of the CO₂ reaction with amine.^[9] In addition, the use of amines can be problematic due to the emission of the utilized volatile components.^[10] Ionic liquids (ILs) are considered as alternatives to amines because of their unique properties such as low melting point, almost unlimited tunability, negligible vapor pressure, and high thermal stability.^[11] By a judicious selection of cation, anion, and functional group, a wide range of ILs can be designed, having different absorption capacities and diverse physical, chemical and even biological properties.^[12] Indeed, several ILs have shown interesting behavior in the absorption and conversion of CO₂.^[13] Specifically, ILs have been applied as both reaction medium and catalyst in high-pressure hydrogenations of carbon dioxide.^[14] As an example, Branko and coworkers performed the hydrogenation of CO₂ to methane using ruthenium nanoparticles (NPs) in imidazolium-based ILs media.^[15] In 2018, Dupont and coworkers produced formic acid (TON = 400) by using ILs such as 1-butyl-3-methylimidazolium acetate (BMI·OAc) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMI·Tf₂N) as catalytic supports for bimetallic RuFe NPs.^[16] In 2020, Hu and coworkers performed CO₂ hydrogenation to formate using imidazole ILs modified copper acetate with improved catalyst turnover numbers (TON > 2,000).^[17] Most recently, Sans and coworkers reported a highly efficient catalytic system for the hydrogenation of gaseous CO₂ to formic acid in buffering ILs.^[18] An overview of previous systems for combined CO₂ capture and hydrogenation to formate and/ or methanol is provided in the Supporting Information (Table S5).


Based on our previous work on CO₂ hydrogenation to formates,^[19] here we report a novel class of ILs-based amino acids and their application in the capture and in situ hydrogenation of CO₂ to formate salts. Although amino acid-based ILs have been used as an efficient and potentially green medium for CO₂ capture,^[20] CCU processes are not described to the best of our knowledge. Complementary to the current industrial setups, the system presented herein offers new and environmentally benign solutions for the capture and utilization of CO₂.

[a] A. Moazezbarabadi,⁺ Dr. D. Wei,⁺ Dr. H. Junge, Prof. Dr. M. Beller
Leibniz-Institut für Katalyse e. V.
Albert-Einstein-Str. 29a, 18059 Rostock (Germany)
E-mail: henrik.junge@catalysis.de
matthias.beller@catalysis.de

[⁺] These authors contributed equally to this work.

 Supporting information for this article is available on the WWW under <https://doi.org/10.1002/cssc.202201502>

 This publication is part of a Special Collection highlighting "The Latest Research from our Board Members". Please visit the Special Collection at chemsuschem.org/collections.

 © 2022 The Authors. ChemSusChem published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

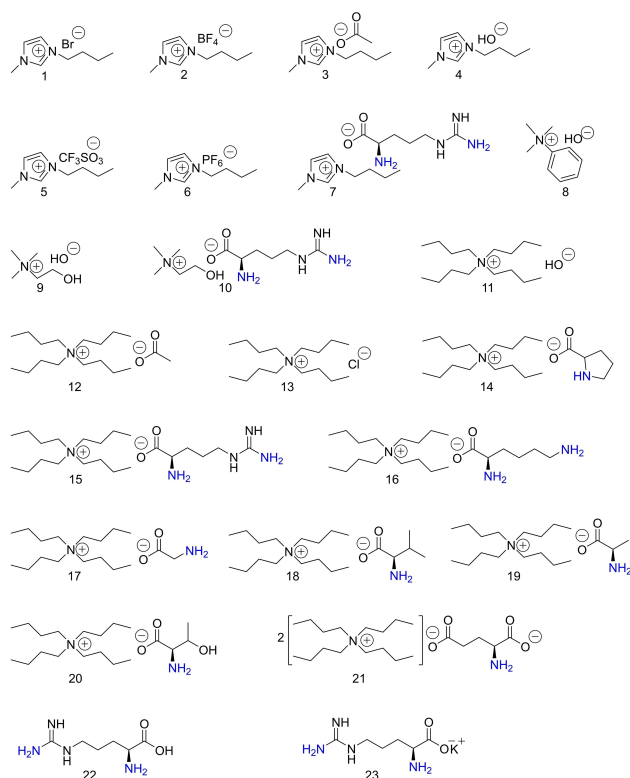
Scheme 1. Investigated absorbents for CO₂ capture in this work.

Table 1. CO₂ capture with absorbents under 2 bar of CO₂.

Entry	Absorbent	CO ₂ (2 bar)	
		H ₂ O, r.t.	Absorbent · CO ₂
		Captured CO ₂ [mmol] ^[a]	Captured CO ₂ /Absorbent ^[b]
1	1	0.62	0.12
2	2	0.75	0.15
3	3	0.87	0.17
4	4	1.05	0.21
5	5	0.78	0.15
6	6	0.86	0.17
7	7	5.62	1.12
8	8	5.01	1.00
9	9	5.34	1.06
10	10	9.21	1.84
11	11	5.80	1.16
12	12	0.76	0.15
13	13	0.61	0.12
14	14	4.30	0.85
15	15	9.70	1.94
16	16	9.02	1.80
17	17	5.40	1.08
18	18	2.04	0.40
19	19	5.38	1.07
20	20	5.00	1.00
21	21	4.40	0.88
22	22	5.20	1.04
23	23	8.50	1.70

Reaction conditions: Absorbent (5.0 mmol), H₂O (5 mL), CO₂ (2 bar), stirred at r.t. (24 °C). [a] Calculated by gravimetric analysis. [b] Calculated by (mmol captured CO₂)/ (mmol absorbent).

Results and Discussion

CO₂ capture with various ionic liquids

We started our investigations by measuring the CO₂ capture capacity of several commercially available ionic liquids (ILs) having different counter ions such as Br⁻, OH⁻, OAc⁻, PF₆⁻, BF₄⁻, CF₃SO₃⁻, etc. (Scheme 1). In a typical experiment, a glass pressure tube was charged with 2 bar CO₂ at room temperature and stirred for 0.5 to 18 h. The absorption capacity was measured by gravimetric analysis (see Supporting Information S2). The high viscosity of ILs however hampers the diffusion of CO₂ inside the bulk of the reaction medium. This increased viscosity becomes evident considering the partial charges at the respective atoms of the -NH₂, to -NH₃⁺, and -NHCO₂⁻ groups.^[21] Furthermore, viscosity increases with the amount of captured CO₂ because of extensive hydrogen bonding. To obviate this issue and improve the efficiency of the process, aqueous solution of ILs were used for the following experiments. A summary of the results is provided in Table 1. First, we tested 1-butyl-3-methylimidazolium-based ILs containing different counter anions (Table 1, entries 1–6), because Sans and others showed that this kind of ILs proved to be very efficient for transformation of CO₂.^[22] However, under our conditions only small amounts of CO₂ were captured, not exceeding 0.21 mmol of CO₂ per mmol of absorbent with the hydroxide anion, very likely a result of its higher basicity compared to OAc⁻, Br⁻ and BF₄⁻, etc. (Table 1, entries 1–6).

To improve the absorption capacity of the IL, alternative cations were tested in combination with the hydroxide anion. Indeed, the amount of mmol CO₂ per mmol absorbent increased, varying from 1.06 for (2-hydroxyethyl) trimethylammonium (Table 1, entry 9), to 1.00 for benzyltrimethylammonium (Table 1, entry 8), and up to 1.16 for tetrabutylammonium as cations, respectively (Table 1, entry 11). The latter was therefore combined with different amino acids (AA) to explore whether this could further increase the amount of captured CO₂. However, no improvement was obtained by replacing hydroxide by glycinate (Table 1, entry 17, 1.08), threoninate (Table 1, entry 20, 1.00), glutamate (Table 1, entry 21, 0.88), valinate (Table 1, entry 18, 0.40), alaninate (Table 1, entry 19, 1.07) and prolinat (Table 1, entry 14, 0.85) anions. Instead, almost 1.80 mmol CO₂ per mmol of absorbent were captured applying lysinate (Table 1, entry 16,) and even 1.94 mmol for arginate (Table 1, entry 15). Apparently, the availability of an extra basic site in the AA side chain clearly expands the capture capacity of the IL. Noteworthy, the tetrabutylammonium arginate [TBA][Arg] turned out to reach a higher amount of absorbed CO₂ than the corresponding 1-butyl-3-methylimidazolium and (2-hydroxyethyl) trimethylammonium containing ILs (Table 1, entries 7 and 10).

Hydrogenation of CO₂ to formate catalyzed by Ru-MACHO-BH in the presence of an absorbent

Having assessed the possibility to effectively capture CO₂ with amino acid tailored ILs, we explored the direct hydrogenation of gaseous CO₂ in the presence of different ILs in the presence of Ru-MACHO-BH, (Table 2), which has been previously found to be highly efficient for this transformation.^[19,23] The reactions were carried out in a mixed solvent H₂O/THF in order to favor catalyst solubility. The autoclave was charged with an initial pressure of 80 bar (H₂ 60 bar, CO₂ 20 bar) and the reaction performed at 80 °C for 24 h. Results are summarized in Table 2. Regardless of the cation, ILs containing Cl⁻, Br⁻ or OAc⁻ were either ineffective (Cl⁻, Br⁻) or barely appropriate (OAc⁻) affording no more than 0.56 moles formate per mole of IL. Very likely this is a result of the very low basicity of these anions and the ensuing reduced CO₂ capture capacity. As expected, improved formate yields were obtained with ILs containing a hydroxide anion (4, 8, 9, 11). However, the cation also plays a role, as the mmol of formate per mmol of absorbent increases from 0.76 for the benzyltrimethylammonium cation (8, Table 2, entry 12), to 0.91 for the (2-hydroxyethyl) trimethylammonium cation (9, Table 2, entry 6), and further to 1.22 applying the tetrabutylammonium cation (11, Table 2, entry 3). Next, we examined the performance of ILs having an arginate counter anion. While generally an improved formate yield was obtained, the best performance was delivered by the combination of arginate with the tetrabutylammonium cation (15), affording 1.91 mmol formate per mmol absorbent (Table 2, entry 1).

For comparison the same reaction was performed in the presence of either arginine or potassium arginate instead of tetrabutylammonium arginate. In both cases the tetrabutyl-

ammonium arginate performed significantly better similar to the CO₂ capture process (compare Table 2, entry 1 with entries 13 and 14), respectively.

Having identified 15 as the IL of choice among those tested, we set out to explore the influence of temperature and solvent composition. While leaving other reaction variables unchanged, experiments were performed at different temperatures in the range 25–145 °C (Table S1). The best yield of formate, in terms of mmol formate per mmol of absorbent, was obtained at 80 °C, both lower and higher temperatures provided inferior results. Furthermore, above 80 °C, non-negligible amounts of formamide started to be formed and the selectivity in formate decreased from 100% at 80 °C to 64% at 145 °C. Therefore, 80 °C was selected for further optimization, providing the best result both in terms of conversion and selectivity.

Organic solvents, other than THF, were tested in combination with water to evaluate their effect on the reaction performance (Table S2). None of the tested co-solvents improved the system performance compared to THF: in fact, the TON recorded with the use of sole THF (Table S2, entry 8, TON=990) was comparable to the one obtained using a mixture of THF/water (Table S2, entry 1, TON=959). This reaction was also scaled up fivefold without any significant drop in formate production (Table S3, entry 6, TON=938). Additionally, to develop a more sustainable system, we also scaled up the reaction in sole water (Table S3, entry 5, TON=833). Next, after having studied all the parameters for CO₂ conversion, we tried to increase the TON of formate by lowering the amount of catalyst. By decreasing the loading of the catalyst from 10 μmol to 0.2 μmol, the TON of formate was considerably increased from 959 to 37,500. (Table S3, entry 1–4). Finally, the reusability of the catalyst was studied (Figure 1). After each run, a new batch of 15 was added to the reaction mixture. Following this procedure, the catalyst was reused for 5 consecutive runs. The amount of produced formate per mmol of absorbent slightly decreased from 1.89 to 1.67, but the total TON reached > 12,700. These results demonstrate the good stability and reusability of the catalyst in the CO₂ hydrogenation process. CO was observed below 1 ppm (< 1 μmol) through GC analysis of the gas mixture after a typical hydrogenation reaction (Figure S9).

Table 2. CO₂ hydrogenation to formate in the presence of different absorbents.

Entry	Absorbent	Formate [mmol] ^[a]	Formate [TON] ^[b]	Ratio Formate/Absorbent
1	15	9.59	959	1.91
2	16	8.84	884	1.76
3	11	6.14	614	1.22
4	13	n.d.	–	–
5	12	2.04	204	0.40
6	9	4.58	458	0.91
7	10	8.80	880	1.76
8	1	n.d.	–	–
9	3	2.82	282	0.56
10	4	1.10	110	0.22
11	7	4.64	464	1.12
12	8	3.83	383	0.76
13	22	3.90	390	0.78
14	23	7.37	737	1.47

Reaction conditions: Absorbent (5.0 mmol), Ru-MACHO-BH (10 μmol), H₂O/THF (5/5 mL), CO₂/H₂ (20/60 bar), 80 °C, 24 h. [a] Determined by ¹H NMR with DMF (250 μL, 3.24 mmol) as internal standard. [b] Calculated by (mmol formate)/(mmol catalyst). n.d. = not detectable.

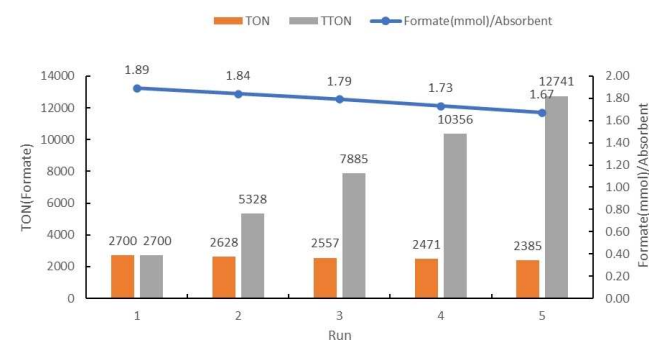


Figure 1. Catalyst reusability profile for the CO₂ hydrogenation to formate in the presence of tetrabutylammonium arginate. Reaction conditions adopted from Table S3, entry 2.

Table 3. Hydrogenation of CO₂ to formate in the presence of [TBA][Arg].

Entry	CO ₂ source	[TBA][Arg] + CO ₂ $\xrightarrow[\text{time (6 h - 10 d)}]{\text{H}_2\text{O, r.t.}}$ [TBA][Arg]•CO ₂		[TBA][Arg]•CO ₂ $\xrightarrow[\text{H}_2 (60 \text{ bar}), 80^\circ\text{C}, 24 \text{ h}]{\text{Ru-MACHO-BH}}$ [TBA][ArgH] ⁺ [HCOO] ⁻			
		Time [h]	Solvent	Captured CO ₂ [mmol]	Formate [mmol] ^[a]	Formate/Absorbent	TON ^[b]
1	CO ₂ (20 bar)	6	H ₂ O/THF	10.1	6.27	1.25	627
2 ^[c]	CO ₂ (20 bar)	24	H ₂ O/THF	45.0	29.25	1.17	585
3 ^[c]	CO ₂ (20 bar)	24	H ₂ O	45.0	26.97	1.07	539
4	CO ₂ (2 bar)	18	H ₂ O/THF	9.7	6.00	1.20	600
5 ^[c]	CO ₂ (2 bar)	96	H ₂ O/THF	44.1	28.79	1.15	575
6 ^[c]	CO ₂ (2 bar)	96	H ₂ O	44.1	26.00	1.04	520
7	Air	120	H ₂ O/THF	5.6	3.05	0.61	305
8 ^[c]	Air	240	H ₂ O/THF	27.2	14.69	0.58	293
9 ^[c]	Air	240	H ₂ O	27.2	12.90	0.51	258

Reaction conditions: CO₂ was firstly captured in aqueous solution of [TBA][Arg] applying the given CO₂ source in 6–240 h. Then hydrogenation was performed (Supporting Information S5), Ru-MACHO-BH (10 μmol), H₂O (5.0 mL), THF (5.0 mL), H₂ (60 bar), 80 °C, 24 h. [a] Determined by ¹H NMR with DMF (250 μL, 3.24 mmol) as internal standard. [b] Calculated by formate [mmol]/catalyst [mmol]. [c] 25 mmol [TBA][Arg], Ru-MACHO-BH (50 μmol).

To make sure that both IL and the catalyst are crucial to promote the hydrogenation of CO₂ to formate, some blank reactions were also performed (Table S4). As expected without IL, catalyst, or CO₂, no formate was detected.

CO₂ capture with tetrabutylammonium arginate and subsequent conversion to formate

Additionally, we tried to convert the captured CO₂ by [TBA][Arg] as described in Table 1 directly to formate at 80 °C and 60 bar H₂ with no external CO₂ addition. Here, CO₂ capture and following in situ hydrogenation was accomplished with 20 bar of CO₂. 10.1 mmol CO₂ were absorbed as carbamate and bicarbonate (Figure S2) yielding 6.27 mmol of formate (Table 3, entry 1, TON = 627). Decreasing the CO₂ pressure to 2 bar resulted in 9.70 mmol absorbed CO₂ (Carbamate and bicarbonate; Figure S3) which was then hydrogenated to 6.00 mmol formate (Table 3, entry 4, TON = 600). To showcase the efficacy of the system in direct air capture (DAC), air was bubbled through a solution of [TBA][Arg] (5 mmol) in water. After 5 days, 5.61 mmol of CO₂ were captured as carbamate (Figure S4), which were hydrogenated to 3.05 mmol formate (Table 3, entry 7, TON = 305). The procedure was then scaled up 5 folds applying either in a mixture of THF/water or sole water (Table 3, entries 2,3,5,6,8,9). In addition, the reusability of the catalyst was studied for the upscaled reaction of CO₂ capture (2 bar) and subsequent hydrogenation in sole water (Figure 2). Following the same procedure, the catalyst was reused for 3 consecutive runs. The amount of produced formate per mmol of absorbent slightly decreased from 1.04 to 0.96, the total TON reached > 7,200.

Conclusion

CO₂ capture and subsequent catalytic hydrogenation to formate was demonstrated using ionic liquids based on amino acid anions as absorbents in an aqueous THF solution. Among the various in situ generated ionic liquids, tetrabutylammonium

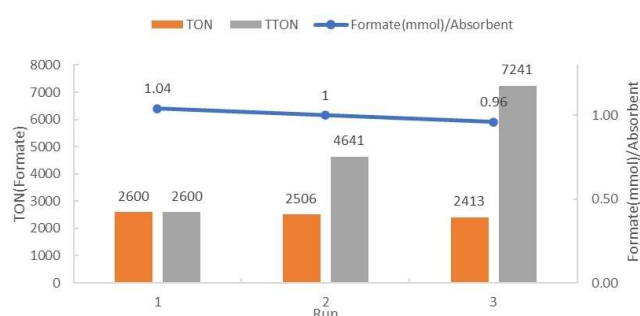


Figure 2. Catalyst reusability profile for the integrated CO₂ hydrogenation to formate. Reaction conditions adopted from Table 3, entry 6. Ru-MACHO-BH (10 μmol).

arginate (15) showed the best CO₂ capture efficiency. This captured CO₂ could be hydrogenated effectively to formate in the presence of the commercially available Ru-MACHO-BH complex. The catalyst reusability was verified with an overall TON of 12,741 in 5 consecutive cycles with no significant decrease in catalytic activity. The CO₂ capture and hydrogenation were upscaled 5-fold achieving an overall TON 7,241 in 3 cycles without organic co-solvent (THF) present. Although 2 bar of pure carbon dioxide were not representative for real capture conditions, the successful application of air as CO₂ source demonstrated the general ability of amino- acid-based ionic liquids for absorption and utilization of carbon dioxide. To make the presented system of practical interest and scalable, currently efforts are ongoing to utilize the absorbent in a catalytic manner, too.

Experimental Section

Procedure for CO₂ capture with 2 bar

A given amount of Absorbent (5.0 mmol) was added in a 25 mL Schlenk tube equipped with stirring bar, followed with 5.0 mL of DI water. Then 2 bar of CO₂ gas was charged into the Schlenk.

Afterwards, the reaction mixture stirred at r.t. for 0.5–18 h. The amount of captured CO₂ was determined gravimetrically.

Capture from ambient air

The absorbent (5.0 mmol) was added in a 25 mL vial followed with 20 mL of DI water, then the indoor air (containing ca. 400 ppm CO₂) was bubbled through the solution using a long needle (1 L min⁻¹). After 5 days, we stopped the air bubbling. 1,4-dioxane (50 μL, 0.58 mmol) was added as an internal standard to the solution, and the mixture was analyzed by ¹³C NMR-quant.

Procedure for the hydrogenation of gaseous CO₂

Ru-MACHO-BH, the absorbent (5.0 mmol) and the solvent (10 mL) were added to a 100 mL autoclave equipped with a magnetic stirring bar. After pressurizing the reactor with CO₂ and H₂ gas, the reactor then heated and stirred on a pre-heated oil bath for 24 h. The reactor was cooled to r.t. DMF (250 μL, 3.24 mmol) was added as an internal standard to the reaction mixture. The reaction mixture was then analyzed by ¹H NMR with a few drops of D₂O (ca. 2 mL) to lock the signals.^[24]

Acknowledgements

We gratefully acknowledge the support from the Federal Ministry of Education and Research (BMBF) and the State of Mecklenburg-Vorpommern. Financial support by the Leibniz Association (Project SUPREME) are also acknowledged. The authors thank the analytical staff of the Leibniz Institute for Catalysis, Rostock, for their excellent service. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Amino Acid · CO₂ capture · Formate · Homogenous Catalyst · Ionic liquid

- [1] a) W. Gao, S. Liang, R. Wang, Q. Jiang, Y. Zhang, Q. Zheng, B. Xie, C. Y. Toe, X. Zhu, J. Wang, *Chem. Soc. Rev.* **2020**, *49*, 8584–8686; b) F. N. Al-Rowaili, U. Zahid, S. Onaizi, M. Khaled, A. Jamal, E. M. AL-Mutairi, *J. CO₂ Util.* **2021**, *53*, 101715.
 [2] P. Panja, *Int. J. Model. Simul.* **2021**, *41*, 209–219.
 [3] K. O. Yoro, M. O. Daramola, in *Advances in carbon capture* (Eds: M. R. Rahimpour, M. Farsi, M. A. Makarem), Elsevier, **2020**, pp. 3–28.
 [4] a) H. Yang, Z. Xu, M. Fan, R. Gupta, R. B. Slimane, A. E. Bland, I. Wright, *J. Environ. Sci.* **2008**, *20*, 14–27; b) M. Mikkelsen, M. Jørgensen, F. C. Krebs, *Energy Environ. Sci.* **2010**, *3*, 43–81; c) C. C. Truong, D. K. Mishra, *J. CO₂ Util.* **2020**, *41*, 101252.

- [5] H. Yang, Z. Xu, M. Fan, R. Gupta, R. B. Slimane, A. E. Bland, I. Wright, *J. Environ. Sci.* **2008**, *20*, 14–27.
 [6] a) X. Xiaoding, J. Moulijn, *Energy Fuels* **1996**, *10*, 305–325; b) H. Yang, Z. Xu, M. Fan, R. Gupta, R. B. Slimane, A. E. Bland, I. Wright, *J. Environ. Sci.* **2008**, *20*, 14–27; c) A. J. Hunt, E. H. Sin, R. Marriott, J. H. Clark, *ChemSusChem* **2010**, *3*, 306–322; d) L. Hamon, H. Leclerc, A. Ghoufi, L. Oliviero, A. Travert, J. Lavalley, T. Devic, C. Serre, *J. Phys. Chem. C* **2011**, *115*, 2047; e) M. Bui, C. S. Adjiman, A. Bardow, E. J. Anthony, A. Boston, S. Brown, P. S. Fennell, S. Fuss, A. Galindo, L. A. Hackett, *Energy Environ. Sci.* **2018**, *11*, 1062–1176; f) D. Wei, R. Sang, A. Moazezbarabadi, H. Junge, M. Beller, *JACS Au* **2022**, *2*, 1020–1031.
 [7] a) C. Song, *Catal. Today* **2006**, *115*, 2–32; b) *Carbon dioxide as chemical feedstock* (Ed: M. Aresta), John Wiley & Sons, Weinheim, Germany, **2010**; c) T. Sakakura, J.-C. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365–2387; d) K. Sordakis, C. Tang, L. K. Vogt, H. Junge, P. J. Dyson, M. Beller, G. Laurenczy, *Chem. Rev.* **2018**, *118*, 372–433; e) S. Kar, A. Goepfert, G. S. Prakash, *Acc. Chem. Res.* **2019**, *52*, 2892–2903; f) W.-H. Wang, X. Feng, M. Bao, *Transformation of carbon dioxide to formic acid and methanol*, Springer, Singapore **2018**; g) Q.-W. Song, Z.-H. Zhou, L.-N. He, *Green Chem.* **2017**, *19*, 3707–3728; h) S. Kar, A. Goepfert, G. S. Prakash, *Acc. Chem. Res.* **2019**, *52*, 2892–2903.
 [8] a) D. M. D'Alessandro, B. Smit, J. R. Long, *Angew. Chem. Int. Ed.* **2010**, *49*, 6058–6082; *Angew. Chem.* **2010**, *122*, 6194–6219; b) P. V. Kortunov, M. Siskin, L. S. Baugh, D. C. Calabro, *Energy Fuels* **2015**, *29*, 5919–5939; c) F. Barzagli, *Int. J. Greenhouse Gas Control* **2011**, *5*, 448–456.
 [9] P. D. Vaidya, E. Y. Kenig, *Chem. Eng. Technol.* **2007**, *30*, 1467–1474.
 [10] K. Veltman, B. Singh, E. G. Hertwich, *Environ. Sci. Technol.* **2010**, *44*, 1496–1502.
 [11] a) M. Aghaie, N. Rezaei, S. Zendeheboudi, *Renewable Sustainable Energy Rev.* **2018**, *96*, 502–525; b) S. Sarmad, J. P. Mikkola, X. Ji, *ChemSusChem* **2017**, *10*, 324–352.
 [12] J. Reichert, S. Maerten, K. Meltzer, A. Tremel, M. Baldauf, P. Wasserscheid, J. Albert, *Sustain. Energy Fuels* **2019**, *3*, 3399–3405.
 [13] a) Z.-Z. Yang, Y.-N. Zhao, L.-N. He, *RSC Adv.* **2011**, *1*, 545–567; b) J. Zhang, J. Sun, X. Zhang, Y. Zhao, S. Zhang, *Greenhouse Gases: Sci. Technol.* **2011**, *1*, 142–159; c) S. K. Shukla, S. G. Khokarale, T. Q. Bui, J.-P. T. Mikkola, *Front. Mater.* **2019**, *6*, 42.
 [14] a) E. Bogel-Lukasik, S. Santos, R. Bogel-Lukasik, M. N. Da Ponte, *J. Supercrit. Fluids* **2010**, *54*, 210–217; b) L. C. Branco, A. Serbanovic, M. N. da Ponte, C. A. Afonso, *ACS Catal.* **2011**, *1*, 1408–1413.
 [15] C. I. Melo, A. Szczepańska, E. Bogel-Lukasik, M. Nunes da Ponte, L. C. Branco, *ChemSusChem* **2016**, *9*, 1081–1084.
 [16] M. I. Qadir, A. Weilhard, J. A. Fernandes, I. de Pedro, B. J. Vieira, J. C. Waerenborgh, J. Dupont, *ACS Catal.* **2018**, *8*, 1621–1627.
 [17] J. Hu, J. Liu, C. Yao, L. Zhou, Y. Wu, Z. Zhang, X. Hu, *Green Chem.* **2021**, *23*, 951–956.
 [18] A. Weilhard, S. P. Argent, V. Sans, *Nat. Commun.* **2021**, *12*, 1–7.
 [19] D. Wei, H. Junge, M. Beller, *Chem. Sci.* **2021**, *12*, 6020–6024.
 [20] a) L. P. Silva, C. Moya, M. Sousa, R. Santiago, T. E. Sintra, A. R. Carreira, J. Palomar, J. A. Coutinho, P. J. Carvalho, *Eur. J. Inorg. Chem.* **2020**, *2020*, 3158–3166; b) N. Noorani, A. Mehrdad, I. Ahadzadeh, *Fluid Phase Equilib.* **2021**, *547*, 113185.
 [21] K. E. Gutowski, E. J. Maginn, *J. Am. Chem. Soc.* **2008**, *130*, 14690–14704.
 [22] a) Y. Wu, Y. Zhao, H. Wang, B. Yu, X. Yu, H. Zhang, Z. Liu, *Ind. Eng. Chem. Res.* **2019**, *58*, 6333–6339; b) K. Simkovičová, M. I. Qadir, N. Žilková, J. E. Olszówka, P. Sialini, L. Kvitek, Š. Vajda, *Catalysts* **2022**, *12*, 516; c) A. Weilhard, S. P. Argent, V. Sans, *Nat. Commun.* **2021**, *12*, 1–7.
 [23] a) S. Kar, J. Kothandaraman, A. Goepfert, G. S. Prakash, *J. CO₂ Util.* **2018**, *23*, 212–218; b) N. M. Rezayee, C. A. Huff, M. S. Sanford, *J. Am. Chem. Soc.* **2015**, *137*, 1028–1031; c) L. Piccirilli, D. Lobo Justo Pinheiro, M. Nielsen, *Catalysts* **2020**, *10*, 773; d) C. Gunanathan, D. Milstein, *Chem. Rev.* **2014**, *114*, 12024–12087.
 [24] A. Dubey, L. Nencini, R. R. Fayzullin, C. Nervi, J. R. Khusnutdinova, *ACS Catal.* **2017**, *7*, 3864–3868.

Manuscript received: August 5, 2022

Revised manuscript received: September 23, 2022

Accepted manuscript online: September 27, 2022

Version of record online: October 27, 2022