



HAL
open science

Efficient CO₂ Sequestration by a Solid-Gas Reaction Enabled by Mechanochemistry: The Case of L-Lysine

Abdal-Azim Al-Terkawi, Frédéric Lamaty, Thomas-Xavier Métro

► **To cite this version:**

Abdal-Azim Al-Terkawi, Frédéric Lamaty, Thomas-Xavier Métro. Efficient CO₂ Sequestration by a Solid-Gas Reaction Enabled by Mechanochemistry: The Case of L-Lysine. 2020. hal-03000893

HAL Id: hal-03000893

<https://hal.science/hal-03000893>

Preprint submitted on 12 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Efficient CO₂ Sequestration by a Solid-Gas Reaction Enabled by Mechanochemistry: The Case of L-Lysine

Abdal-Azim Al-Terkawi, Frédéric Lamaty, Thomas-Xavier Métro*

Institut des Biomolécules Max Mousseron (IBMM), UMR 5247, Université de Montpellier, CNRS, ENSCM, Campus Triolet, Place Eugène Bataillon, 34095 Montpellier cedex 5, France

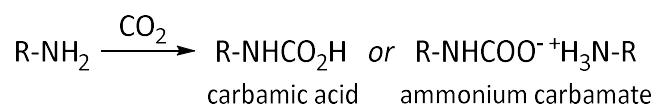
E-mail of the corresponding author: thomas-xavier.metro@umontpellier.fr

Abstract

This study describes an efficient and solvent-free method for the regioselective production of L-lysine ammonium ϵ -carbamate by ball-milling L-lysine under an atmosphere of CO₂. The regioselective formation of L-lysine ammonium ϵ -carbamate by this mechanochemical approach was confirmed by a complete analytical study, including $^1\text{H}\rightarrow^{13}\text{C}$ and $^1\text{H}\rightarrow^{15}\text{N}$ CP MAS NMR measurements as well as liquid NMR analysis, powder X-ray diffraction, thermal analysis, and elemental analysis. Time of milling, rotational speed, milling material, and liquid assistants were screened, while the reversibility of the process was assessed. This milling approach was compared with the syntheses in aqueous solution and in the solid-state without agitation. In addition to be regioselective, the synthesis by solvent-free mechanochemistry was found to be much faster than the other approaches while producing lot less waste.

Introduction

The immense production of CO₂, due to humans and industrial activities, and its steady accumulation in the atmosphere is a significant cause of global warming, which is expected to reach 1.5 °C between 2030 and 2052, triggering climate-related risks for nature and humans. Therefore, a massive reduction or zero-CO₂ emission is crucial to prevent further climate-related damages.¹ Besides, CO₂ is an abundant, economic, and renewable carbon source that could be captured and used for the production of various materials thereby avoiding its greenhouse effect.²⁻⁷ For instance, CO₂ is well-known to react with amines, leading to the formation of carbamic acids or ammonium carbamates depending on, among other factors, structures of amines and solvents (**Equation 1**).^{2,8,9}



Equation 1: Formation of a carbamic acid or an ammonium carbamate from an amine and CO₂.

This reactivity has been utilised at the industrial scale to capture CO₂ issuing from fossil fuel-burning power plants.¹⁰⁻¹⁴ Unfortunately, these processes are limited by their cost due to the energy needed at the CO₂ regeneration step, by equipment corrosion, volatility and stability of the amines along with environmental issues.¹¹⁻¹⁷ While the predominant processes capturing CO₂ rely on the use of toxic alkanolamines as chemical sorbents, some research groups have studied the reactivity of CO₂ with amino groups of innocuous α -amino acids and derivatives to form carbamates.¹⁸⁻²³ Of note, vast majority of these reactions are performed in a liquid phase, mostly using water as a solvent. Using a solvent is the standard approach to homogenize reaction mixtures and to facilitate agitation by traditional stirring systems, yet lowering the theoretical maximum speed of reactions by moving the reactants away from each other. To the best of our knowledge, only one example of solvent-free reactivity between amino acid derivatives and CO₂ has been described in the literature: the group of Limbach has studied by solid-state NMR the formation of carbamates issuing from the exposition of solid poly-L-lysine to atmospheric CO₂.^{24,25} In this case, the reactivity between poly-L-lysine and CO₂ may have been seriously hampered by mass transfer limitations. To avoid such limitations, many research groups have turned to mechanochemistry, predominantly ball-milling, performing an extraordinarily wide array of reactions between solids in the total absence of

solvents.^{26–30} Additionally, mechanochemistry is capable of modifying selectivity when compared to solvent-based synthesis and giving access to otherwise inaccessible compounds.³¹ Such features led the IUPAC to identify mechanochemistry as one of the top ten technologies that will change the world.³² While mechanochemistry is now commonly used for the chemical transformation of solids sometimes involving liquids, it has been used only scarcely with gaseous reactants,³³ yet with very high efficiency in specific cases.³⁴ Examples describing the use of ball-milling to convert CO₂ are even rarer.^{35–37} Besides, L-lysine is an innocuous and essential α -amino acid, produced at more than a million metric tons per year and of paramount importance for animal feed, pharmaceutical, and cosmetic industries.³⁸ This situation prompted us to study the reactivity of L-lysine with gaseous CO₂ under ball-milling. The results of this approach were compared with syntheses in aqueous solution and with synthesis in the absence of both solvent and agitation. To the extent of our knowledge, the present work is the first study on carbamates formation by milling an amino acid with CO₂.

Results and Discussion

Reactivity and selectivity

In a typical milling experiment, 500 mg of commercially available L-lysine was milled in a planetary mill for 5 h under 5 bar of CO₂ (a 20 ml ZrO₂-reactor containing 80 ZrO₂-balls of 5 mm diameter was used), leading to the formation of a white powder that was recovered directly from the milling reactor and first analysed by thermogravimetry measurements. The corresponding thermoanalytical curve depicted a mass loss of -12.4% between 75 °C and 175 °C which was attributed to the release of one CO₂ molecule (calc. 12.42%) from an ammonium-carbamate ions pair and thereby confirming the formation of the carbamate bond during milling. The mass loss observed up to 75 °C (-5.1%) was assigned to the release of one water molecule (calc. 5.08%), indicating that the ammonium-carbamate ions pair was obtained as a monohydrate (0.5H₂O per one L-lysine molecule). These results were consolidated by the elemental analysis that was in agreement with the formation of an ammonium carbamate monohydrate (see **Figure S3** and **Table S2** for details). The formation of a carbamate bond was further confirmed by ¹H→¹³C CP MAS NMR spectrum that depicted a carbon signal at $\delta = 165$ ppm (**Figure 1**, red spectrum).

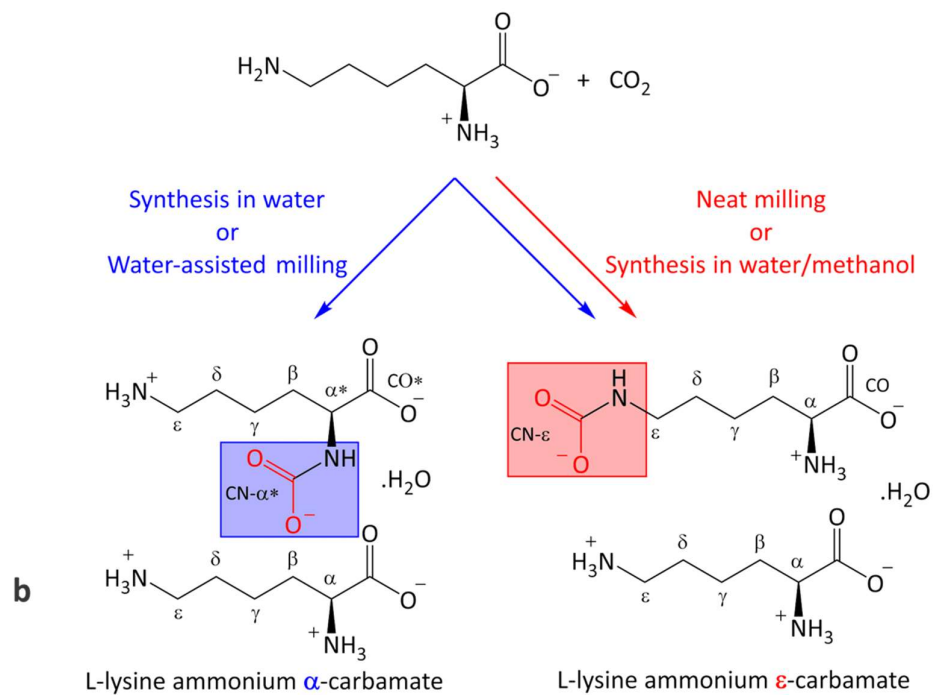
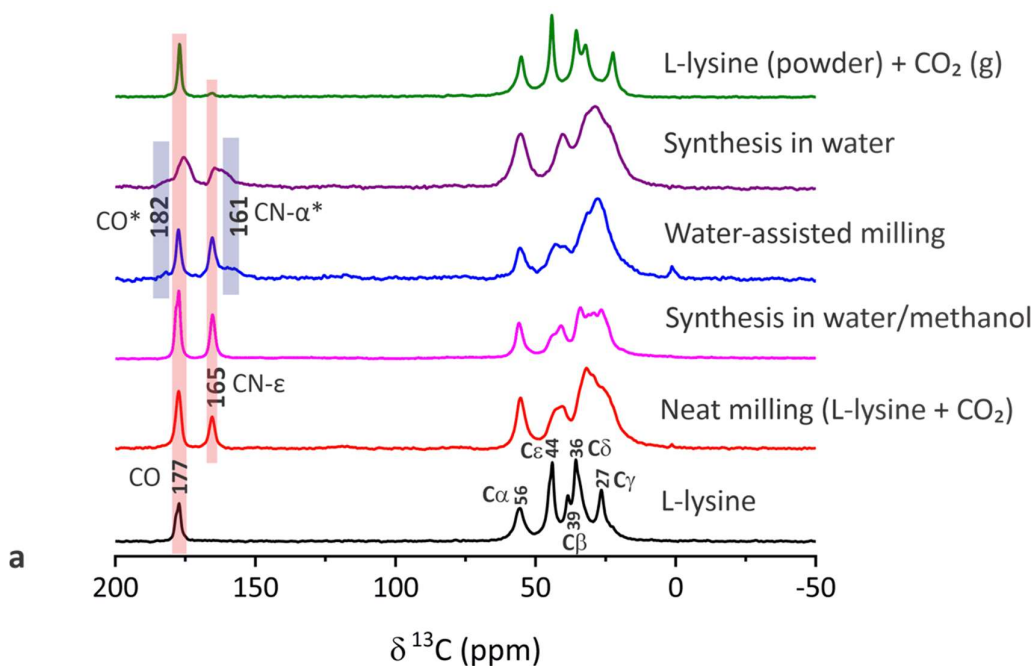


Figure 1: (a) $^1\text{H} \rightarrow ^{13}\text{C}$ CP MAS NMR spectra of L-lysine (black spectrum) and of the products obtained by the reaction of L-lysine with CO_2 gas under neat milling conditions (red spectrum), synthesis in water/methanol (magenta spectrum), water-assisted milling (blue spectrum), bubbling CO_2 gas into an aqueous solution of L-lysine followed by water evaporation (purple spectrum), storing L-lysine (powder) under CO_2 gas atmosphere for 15 days (green spectrum). (b) The proposed molecular structures of L-lysine ammonium ϵ -carbamate (obtained by neat milling and synthesis in water/methanol) and L-lysine ammonium α - and ϵ -carbamates (obtained by water-assisted milling and synthesis in water). *Color codes:* The ϵ -carbamate bond is shaded in red, and the α -carbamate bond is shaded in blue.

Noteworthy, only one peak was observed in the carbamate region, strongly suggesting the newly formed carbamate bond was selectively installed on one of the two available positions only (α -NH₂ or ε -NH₂). This result was confirmed by $^1\text{H} \rightarrow ^{15}\text{N}$ CP MAS NMR experiment showing only one peak at $\delta = 88$ ppm corresponding to a nitrogen atom engaged in a carbamate bond (**Figure 2**, red spectrum).

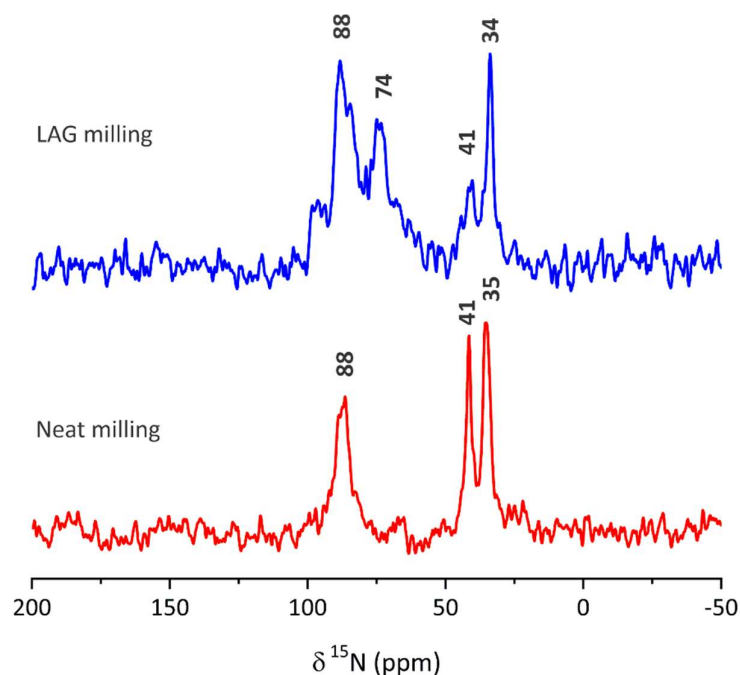


Figure 2: $^1\text{H} \rightarrow ^{15}\text{N}$ CP MAS NMR of the products obtained by the reaction of L-lysine with CO₂ gas under neat milling conditions (red spectrum) and under LAG conditions (50 μL H₂O/500 mg L-lysine) (blue spectrum).

On the $^1\text{H} \rightarrow ^{13}\text{C}$ CP MAS NMR spectrum (**Figure 1**, red spectrum), the single carbon signal at $\delta = 178$ ppm displaying a similar chemical shift to the signal of the L-lysine carboxylate ($\delta = 177$ ppm, black spectrum), strongly suggested that the carbamate bond was not installed on the α -NH₂, but on the ε -NH₂. These results were then compared with the L-lysine ammonium carbamate obtained by bubbling CO₂ for 4h into an aqueous solution of L-lysine (500 mg of L-lysine dissolved in 5 ml D₂O) followed by concentration to dryness to remove water. The $^1\text{H} \rightarrow ^{13}\text{C}$ CP MAS NMR spectrum of the corresponding L-lysine ammonium carbamate (**Figure 1**, purple spectrum) depicted a peak at $\delta = 165$ ppm and a high shoulder at $\delta = 161$ ppm indicative of the formation of two different carbamates installed at the α -NH₂ and the ε -NH₂ positions, contrary to neat milling. This spectrum also depicted two signals corresponding to a carboxylate: a peak at $\delta = 178$ ppm (similar to the carboxylate of L-lysine, **Figure 1**, black

spectrum) and a shoulder at 182 ppm that can be assigned to the carboxylate bearing a carbamate on the α -NH₂. As this later peak is not visible on the $^1\text{H}\rightarrow^{13}\text{C}$ CP MAS NMR spectrum of the L-lysine ammonium carbamate obtained by neat milling, this is an additional proof that neat milling led to the formation of the L-lysine ammonium carbamate on the ε -NH₂ position only (**Figure 1**, red spectrum). In addition to be a regioselective process, neat milling provided L-lysine ammonium ε -carbamate in quantitative yields as for every reaction conditions screened (all the experimental conditions are summarized in **Table S1**), the obtained powders were analytically pure after being recovered directly from the milling reactor without further treatment. Due to the poor crystallinity of the obtained powders, *ab initio* structures determination of carbamates starting from the powder X-ray diffraction (PXRD) data was unfortunately not possible. Efforts for improving polycrystallinity or the growth of single crystals did not succeed so far. Neat milling was not the only strategy enabling to obtain L-lysine ammonium ε -carbamate regioselectively. Indeed, a patent authored by Bru in 1980 described the synthesis of L-lysine ammonium ε -carbamate by reacting CO₂ with L-lysine solubilized in a 1:5 water/methanol mixture.⁴¹ Although the original paper was not providing any experimental proof of the regioselectivity of the reaction, in our hands the corresponding protocol produced L-lysine ammonium ε -carbamate regioselectively as indicated by $^1\text{H}\rightarrow^{13}\text{C}$ CP MAS NMR spectrum (**Figure 1**, magenta spectrum). Yet, in addition to require the use of the highly toxic MeOH, this strategy necessitated more experimental time than neat milling (*vide infra*). One could explain the selectivity of the reaction under neat milling by the crystalline structure of L-lysine. Indeed, in the crystal structures reported by Harris and coworkers,^{39,40} L-lysine molecules are found as zwitterions where the α -nitrogen atom is protonated (as α -NH₃) while the ε -NH₂ is not (yet involved in a hydrogen-bonding network (HBN) with water); this difference could explain the higher reactivity of the ε -nitrogen atom. This selectivity related to the crystal structure of L-lysine is also a strong indication that the carbamate formation during neat milling is a solid-state process, and that the presence of crystallized water in L-lysine hemihydrate is clearly not sufficient to induce the formation of both α - and ε -carbamates. On the opposite, the protophilic character of water could explain the non-selectivity of the formation of the carbamate when synthesis is performed in water. The selective formation of the ε -carbamate in a water/methanol mixture could there be explained by the precipitation/crystallisation which is known to be a potentially selective process.

Speed of reaction

The influence of milling time on the formation of L-lysine ammonium ϵ -carbamate was next investigated (**Table S1**). To our delight, conversion of L-lysine was completed after a reduced milling time of only 5 min, indicating that the reaction is very rapid. Comparatively, synthesis in water was much slower, which was explained by the formation of carbonate/bicarbonate ions as the kinetic products resulting from the reaction of water with CO_2 , as indicated by the typical carbon signals at about $\delta = 160$ ppm (**Figure 3**, red ^{13}C NMR spectrum). The carbon signals related to the carbamate bond formation start to appear only after 48h of reaction (**Figure 3**, blue spectrum, peaks at $\delta = 164.8$ and 163.7 ppm). Alternatively, a mixture of L-lysine ammonium α - and ϵ -carbamates could be isolated after removing water under reduced pressure, which is yet known to be an energy-intensive process (**Figure 3**, purple spectrum).

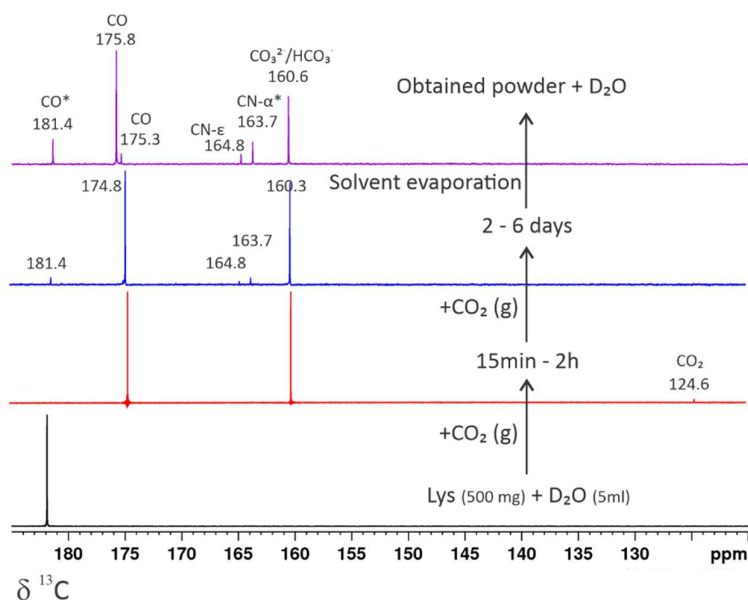


Figure 3: The ^{13}C NMR spectra of L-lysine solubilized in D_2O (black spectrum), bubbling CO_2 (g) into the aqueous L-lysine for 15 min to 2h (red spectrum), bubbling CO_2 (g) into the aqueous solution for 2-6 days (blue spectrum), and after the solvent evaporation (purple spectrum).

^{13}C NMR analysis of a pure sample of L-lysine ammonium ϵ -carbamate also displays a small peak corresponding to the formation of carbonate/bicarbonate ions ($\delta = 161$ ppm) almost immediately after dissolution in D_2O , confirming that the formation of ammonium carbamates of L-lysine is a reversible process in water.^{42,43}

Structural analysis by liquid NMR

The rapid formation of carbonate/bicarbonate ions after solubilisation of L-lysine ammonium carbamates in D₂O did not prevent homo- and hetero-nuclear 2D liquid NMR measurements to give relevant information on the structure of L-lysine ammonium carbamates in D₂O. On the contrary to ¹H→¹³C CP MAS NMR experiment, the ¹H/¹³C HMBC measurement of L-lysine ammonium ε-carbamate after solubilisation in D₂O (**Figure 4**) depicted two carbon signals at δ = 164 and 165 ppm, indicating the formation of two different carbamate bonds. This difference could be explained by migrations of the carbamate bonds between ε-NH₂ and α-NH₂ through the intermediate formation of solubilised CO₂. The two cross-peaks of the proton signal at δ = 3.8 (label: Hα*) with the carbamyl carbon signal at δ = 164 ppm (CN-α*) and the carboxylate carbon at δ = 181 ppm (CO*) indicates the formation of the α-carbamate ion. Furthermore, the cross-peak between the proton Hα (δ = 3.4 ppm) and the carboxylate carbon CO (δ = 177 ppm) is attributed to the formation of α-ammonium ion. On the other hand, the cross-peak between the proton signal at δ = 2.85 ppm (Hε) and the carbamyl signal at δ = 165 ppm (CN-ε) indicates the formation of ε-carbamate ion. These measurements suggest that, in water, both the α- and ε-carbamates are individually formed in two different lysine molecules, as depicted in **Figure 1b**. The proton-carbon cross-peak at δ = 3.5 ppm (Hα+)/176 ppm (CO+) is attributable to the protons exchange between α-amino and carboxylate groups (⁺H₃N-C_αHR-COO⁻ ↔ H₂N-C_αHR-COOH) indicated by the minimal chemical shift between both carboxylate groups (Δδ = 1 ppm).

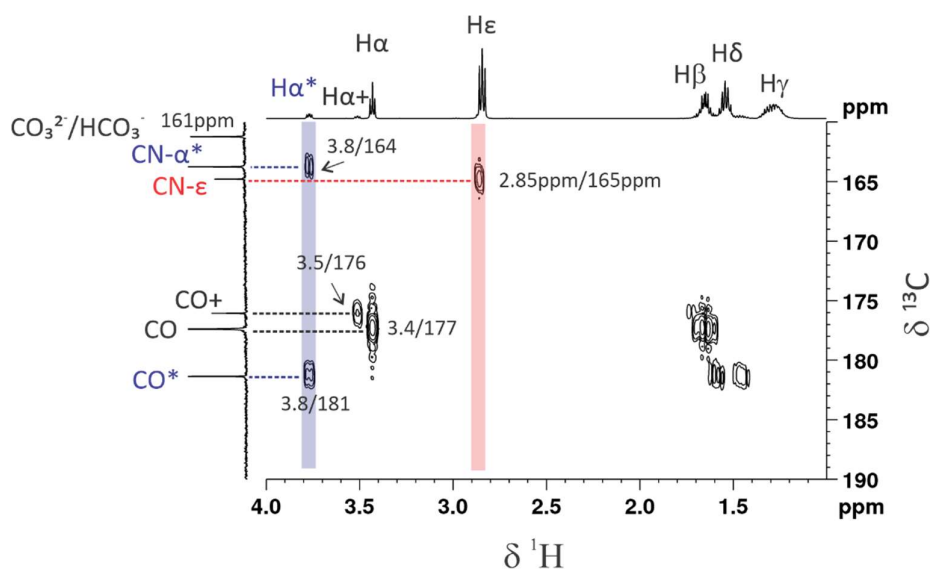


Figure 4: The ¹H/¹³C HMBC spectrum of L-lysine ammonium α- and ε-carbamates obtained by milling.

Influence of liquid additives

We next investigated the influence of liquid additives on the formation of L-lysine ammonium ϵ -carbamate by ball-milling. Indeed, previous studies on solution-based reactions showed that the nature of the solvent could influence the selectivity outcome of the reaction between amino-functionalized samples and CO₂ in solution.^{8,44} In mechanochemistry, the use of a liquid additive during milling, known as Liquid-Assisted Grinding (LAG), is known to be capable of sharply accelerating the reactions, improving the crystallinity of the resulting powder products and modifying the polymorphic outcome.^{45–50} In our case, adding a small amount of water (50 μ l H₂O/500 mg L-lysine) led to the formation of the carbamate bond on the two positions, as indicated by the peak at $\delta = 165$ ppm and the shoulder at $\delta = 161$ ppm in ¹H→¹³C CP MAS measurement (**Figure 1**, blue spectrum). In addition, ¹H→¹⁵N CP MAS measurement displayed two peaks at $\delta = 88$ ppm and $\delta = 74$ ppm in the carbamate region (**Figure 2**, blue spectrum). The formation of the carbamates at both the α - and ϵ -NH₂ positions even when minimal amounts of water are present during the synthesis is a clear indication that the total absence of “free” water during milling (as opposed to crystallised water present in the starting material) is necessary to have a selective formation of the carbamate at the ϵ -NH₂ position. Yet, contrary to neat milling, grinding with protophilic solvents such as water or DMSO as liquid assistants provided L-lysine ammonium carbamates with higher crystallinity (**Figure S5**, red and blue patterns) than the products obtained by neat milling (**Figure S5**, black pattern), as indicated by powder X-ray diffraction. However, milling with non-protophilic CH₂Cl₂ as liquid assistant did not clearly improve the crystallinity of the final powder (**Figure S5**, cyan pattern).

Reactivity in the solid state without agitation

Besides, to understand the role of agitation during the milling process, gaseous CO₂ was flushed over powders of L-lysine for 4h without any agitation, followed by storing the powders under a CO₂ atmosphere at ambient pressure for 15 days. ¹H→¹³C CP MAS NMR measurements of the resulting powder indicated the incomplete conversion of L-lysine to the corresponding ammonium carbamate as indicated by the very small peak at $\delta = 165$ ppm (**Figure 1**, green spectrum). This latter result indicates that the reactivity between L-lysine and CO₂ is leading to a “negative feedback” as theorized by Boldyreva,²⁸ confirming that the

grinding process is necessary for the rapid conversion of L-lysine to the corresponding ammonium carbamate.

Environmental impact

We next compared the production of waste by the three protocols enabling to produce L-lysine ammonium carbamates from L-lysine and CO₂: neat milling, synthesis in water and synthesis in water/MeOH. The E-factor was calculated for each of these three approaches and are reported in **Table 1**.⁵¹

Table 1: E-factors for the synthesis of L-lysine ammonium carbamates by neat milling, synthesis in water, and synthesis in water/methanol (see Supporting Information for details of the calculations).

Type of synthesis	E-factor
Neat milling	0.08
Synthesis in water	8.8
Synthesis in water/methanol	7.4

Comparing the E-factors clearly indicates that neat milling is the process that enables the lowest production of waste, a hundred times less than more classical syntheses in water or water/methanol. This superiority is clearly due to the absence of bulk solvent during neat milling.

Stability and reversibility

Next, the thermal stability of L-lysine ammonium ϵ -carbamate and the reversibility of the formation of this carbamate were assessed. After being stored under ambient conditions for several months, L-lysine ammonium ϵ -carbamate showed no analytical differences with the freshly prepared compounds, indicating its good stability under ambient conditions. The thermal treatment of L-lysine ammonium ϵ -carbamate at 175 °C for 1h or the addition of a few drops of aqueous DCl cleaved the carbamate bond. The release of gaseous CO₂ was indicated by the continuous formation of bubbles while adding aqueous DCl on the aqueous solutions of L-lysine ammonium ϵ -carbamate, in addition to the disappearance of the carbamate signals in the ¹³C NMR spectra (**Figure 5**, red spectrum) (by thermal treatment at 175 °C, **Figure 5**, green spectrum). The comparisons of ¹³C NMR spectra in **Figure S6** indicate

the presence of small quantities of non-identified products after the DCI treatments, while these products are present in smaller quantities after the thermal treatment. The latter spectrum is similar to the ^{13}C NMR spectrum of L-lysine, which clearly indicates that the carbamates formation by milling L-lysine with CO_2 is a reversible process upon heating at 175 $^\circ\text{C}$.

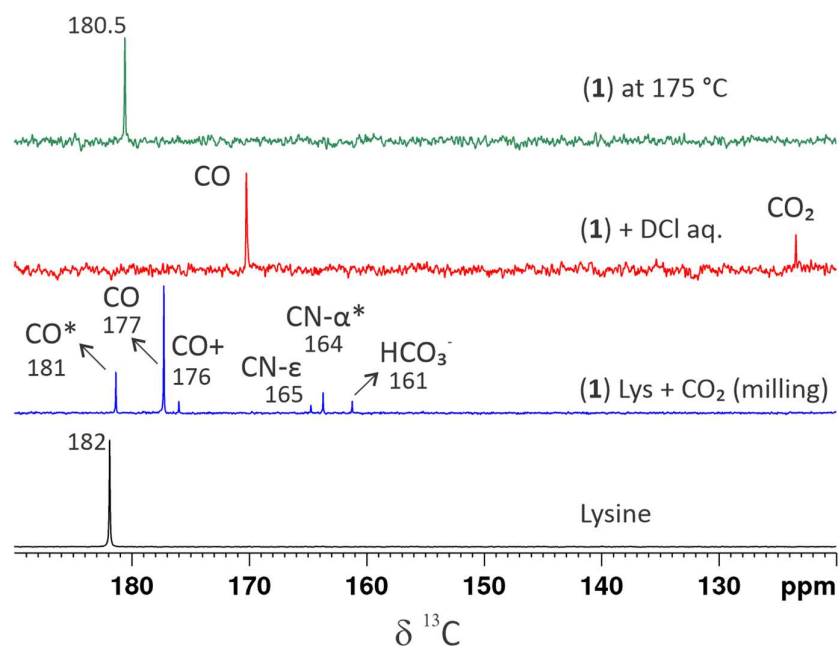
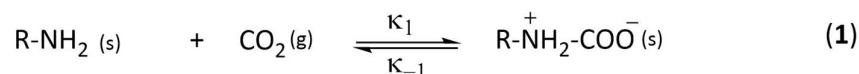


Figure 5: The ^{13}C NMR spectra of L-lysine ammonium ϵ -carbamate as-synthesized, and after post-treatment (in D_2O). L-lysine (black spectrum) depicts the carbon signal of carboxylate group ($\delta = 182$ ppm). The carbamate bond of L-lysine ammonium ϵ -carbamate obtained by milling (blue spectrum) is cleaved after treatments by adding aqueous DCI (red spectrum) or by thermal treatment at 175 $^\circ\text{C}$ for 1h (green spectrum).

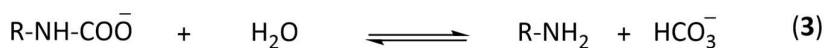
Mechanism

In literature, thorough kinetic studies were described and mainly two mechanisms were proposed to describe the reaction between alkylamines and alkanolamines with CO_2 : termolecular mechanism and zwitterion mechanism.^{52–54} The latter mechanism is commonly used to explain CO_2 reaction with amino acids.^{20,22,23} In this proposed reaction pathway (**Scheme 1**), the carbamate formation is explained by the nucleophilic attack of the nitrogen on the electrophilic carbon of the carbon dioxide molecule forming a zwitterion (Equation 1). Second, another amino-functionalized molecule act as a weak base for the formation of ammonium carbamate ions pair (Equation 2). Such mechanism could also explain the formation of the carbamates obtained by milling in the absence or quasi-absence of added liquids.



Scheme 1: The proposed zwitterion mechanism for the formation of ammonium carbamate by milling L-lysine (introduced as R-NH₂) under a CO₂ atmosphere.

In solution-based reactions, it has been reported that carbamic acids of amines and lysine peptide are selectively generated in polar aprotic solvents.^{44,20} For our experiments, using LAG conditions of solvents such as DMSO and DCM led only to the formation of ammonium carbamates of L-lysine as indicated by ¹³C NMR spectra (**Figure S6**). The latter result can be rationalized by the poor solubility of L-lysine in the organic solvents taking into account that the previously reported experiments were performed on α -amino acids completely solubilized in organic solvents. However, and due to the protogenic and nucleophilic character of water, dissolving in water the carbamate products obtained by milling leads to the formation of carbonate/bicarbonate anions as depicted by ¹³C NMR analysis (**Figure S5**). Here, it is important to distinguish between the synthesis of carbamates obtained by neat milling the solid L-lysine with CO₂ and the carbamates formed by bubbling the CO₂ in aqueous solutions containing L-lysine (**Scheme 2**). The carbamates obtained by neat milling depicts only partial conversion to carbonate/bicarbonate anions when solubilized in water (Equation 3). On the opposite, bubbling gaseous CO₂ into a solution of L-lysine in water leads first to the formation of carbonate/bicarbonate anions (Equation 4) and way after to the formation of the carbamate compounds (2-6 days). Comparatively, the rapid appearance (few minutes) of a precipitate of L-lysine ammonium ϵ -carbamate after bubbling CO₂ in a solution of L-lysine in a 1:5 mixture of water/methanol might indicate that the precipitation mechanism prevails over the formation of the carbonate/bicarbonate anions. Overall, it is strongly suggested that the absence of the added water during neat milling prevents the competitive formation of the carbonate/bicarbonate anions, which would explain the much faster formation of the carbamate by milling than during synthesis in water.



Scheme 2: The conversion of carbamate to carbonate/bicarbonate reaction (equation 3), the formation of ammonium-bicarbonates by dissolving gaseous CO₂ in aqueous amine-containing substrate (eq. 4), and the formation of bicarbonate by dissolving CO₂ in water (eq. 5).

Conclusion

L-lysine ammonium ϵ -carbamate can be easily, rapidly and selectively produced in quantitative yields by the solid-gas mechanochemical reaction of L-lysine with CO₂. While the same regioselectivity could be obtained by performing the synthesis in a water/methanol mixture, synthesis by neat milling discarded the use of the highly toxic methanol. The process is highly robust as the analytically pure carbamate was formed in a wide range of operational conditions (reaction time, rotational speed, milling material). In addition, this milling approach was much faster than synthesis by bubbling CO₂ into a solution of L-lysine in water, most probably due to the absence of competitive formation of the carbonate/bicarbonate anions. Neat milling also proved to be the process that produces the least waste, as indicated by a very low E-factor of 0.08. Overall, the present work introduces a solid-gas reaction enabled by mechanochemistry as a rapid, regioselective and clean method for the chemical conversion of gaseous CO₂ into L-lysine ammonium ϵ -carbamate via its direct and solvent-free reaction with L-lysine. This study opens doors to future uses of other innocuous amines as efficient sorbents for CO₂ sequestration under solvent-free mechanochemical conditions, which are currently under investigations in our laboratory.

Supporting Information

PDF file: Experimental protocols, liquid NMR spectra, PXRD data, elemental analysis, and thermal analysis measurements.

Acknowledgments

Centre National de la Recherche Scientifique (CNRS), CNRS National Institute of Chemistry (grant to T.-X. M. through EMERGENCE@INC2018 call for proposals) and Université de Montpellier are acknowledged for financial support. We also thank the following colleagues for technical support: Aurélien Lebrun and Karine Parra (liquid NMR), Philippe Gaveau, and Emmanuel Fernandez (MAS NMR), Amine Geneste and Romain Tavernier (thermal analysis), Dominique Granier (powder XRD) and Magalie Lefeuvre (elemental analysis).

References

- (1) Masson-Delmotte, V.; Zhai, P.; Pörtner, H.-O.; Roberts, D.; Skea, J.; Shukla, P. R.; Pirani, A.; Moufouma-Okia, W.; Péan, C.; Pidcock, R.; et al. Global Warming of 1.5°C An IPCC Special Report. *Rep. Intergov. Panel Clim. Change* **2018**, *265*, 37–46.
- (2) Belli Dell'Amico, D.; Calderazzo, F.; Labella, L.; Marchetti, F.; Pampaloni, G. Converting Carbon Dioxide into Carbamate Derivatives. *Chem. Rev.* **2003**, *103* (10), 3857–3897. <https://doi.org/10.1021/cr940266m>.
- (3) Sakakura, T.; Choi, J. C.; Yasuda, H. Transformation of Carbon Dioxide. *Chem. Rev.* **2007**, *107* (6), 2365–2387. <https://doi.org/10.1021/cr068357u>.
- (4) Riduan, S. N.; Zhang, Y. Recent Developments in Carbon Dioxide Utilization under Mild Conditions. *Dalton Trans.* **2010**, *39* (14), 3347–3357. <https://doi.org/10.1039/b920163g>.
- (5) Aresta, M. Carbon Dioxide as a Direct Chemical Feedstock. **2010**, 394. <https://doi.org/10.1002/9783527629916>.
- (6) Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. Using Carbon Dioxide as a Building Block in Organic Synthesis. *Nat. Commun.* **2015**, *6*, 1–15. <https://doi.org/10.1038/ncomms6933>.
- (7) Song, Q.-W.; Zhou, Z.-H.; He, L.-N. Efficient, Selective and Sustainable Catalysis of Carbon Dioxide. *Green Chem.* **2017**, *19* (16), 3707–3728. <https://doi.org/10.1039/C7GC00199A>.
- (8) Masuda, K.; Ito, Y.; Horiguchi, M.; Fujita, H. Studies on the Solvent Dependence of the Carbamic Acid Formation from ω -(1-Naphthyl)Alkylamines and Carbon Dioxide. *Tetrahedron* **2005**, *61* (1), 213–229. <https://doi.org/10.1016/j.tet.2004.10.033>.
- (9) Rudkevich, D. M.; Xu, H. Carbon Dioxide and Supramolecular Chemistry. *Chem. Commun.* **2005**, *1* (21), 2651–2659. <https://doi.org/10.1039/b500318k>.
- (10) Rochelle, G. T. Amine Scrubbing for CO₂ Capture. *Science* **2009**, *325* (5948), 1652–1654. <https://doi.org/10.1126/science.1176731>.
- (11) MacDowell, N.; Florin, N.; Buchard, A.; Hallett, J.; Galindo, A.; Jackson, G.; Adjiman, C. S.; Williams, C. K.; Shah, N.; Fennell, P. An Overview of CO₂ Capture Technologies. *Energy Environ. Sci.* **2010**, *3* (11), 1645–1669. <https://doi.org/10.1039/c004106h>.

- (12) Raynal, L.; Bouillon, P. A.; Gomez, A.; Broutin, P. From MEA to Demixing Solvents and Future Steps, a Roadmap for Lowering the Cost of Post-Combustion Carbon Capture. *Chem. Eng. J.* **2011**, *171*, 742–752. <https://doi.org/10.1016/j.cej.2011.01.008>.
- (13) Dutcher, B.; Fan, M.; Russell, A. G. Amine-Based CO₂ Capture Technology Development from the Beginning of 2013—A Review. *ACS Appl. Mater. Interfaces* **2015**, *7* (4), 2137–2148. <https://doi.org/10.1021/am507465f>.
- (14) Heldebrant, D. J.; Koech, P. K.; Glezakou, V. A.; Rousseau, R.; Malhotra, D.; Cantu, D. C. Water-Lean Solvents for Post-Combustion CO₂ Capture: Fundamentals, Uncertainties, Opportunities, and Outlook. *Chem. Rev.* **2017**, *117* (14), 9594–9624. <https://doi.org/10.1021/acs.chemrev.6b00768>.
- (15) The Norwegian Institute of Public Health (NIPH). *Health Effects of Amines and Derivatives Associated with CO₂ Capture: Nitrosamines and Nitramines*; 2011; pp 1–15.
- (16) Ghayur, A.; Verheyen, T. V.; Meuleman, E. Biological and Chemical Treatment Technologies for Waste Amines from CO₂ Capture Plants. *J. Environ. Manage.* **2019**, *241*, 514–524. <https://doi.org/10.1016/j.jenvman.2018.07.033>.
- (17) Monoethanolamine (MEA), the Most Widely Used Amine to Capture CO₂ at the Industrial Scale, Is Corrosive and Highly Toxic According to Regulation EC No 1272/2008.
- (18) Zhang, J.; Zhang, S.; Dong, K.; Zhang, Y.; Shen, Y.; Lv, X. Supported Absorption of CO₂ by Tetrabutylphosphonium Amino Acid Ionic Liquids. *Chem. - Eur. J.* **2006**, *12* (15), 4021–4026. <https://doi.org/10.1002/chem.200501015>.
- (19) Stastny, V.; Anderson, A.; Rudkevich, D. M. Supramolecular Structures from Lysine Peptides and Carbon Dioxide. *J. Org. Chem.* **2006**, *71*, 8696–8705. <https://doi.org/10.1021/jo061144k>.
- (20) Yamamoto, Y.; Hasegawa, J. Y.; Ito, Y. Kinetic Investigation on Carbamate Formation from the Reaction of Carbon Dioxide with Amino Acids in Homogeneous Aqueous Solution. *J. Phys. Org. Chem.* **2012**, *25*, 239–247. <https://doi.org/10.1002/poc.1900>.
- (21) Saravanamurugan, S.; Kunov-kruse, A. J.; Fehrmann, R.; Riisager, A. Amine-Functionalized Amino Acid-Based Ionic Liquids as Efficient and High-Capacity Absorbents for CO₂. *Chem SusChem* **2014**, *7*, 897–902. <https://doi.org/10.1002/cssc.201300691>.
- (22) Shen, S.; Yang, Y. N.; Bian, Y.; Zhao, Y. Kinetics of CO₂ Absorption into Aqueous Basic Amino Acid Salt: Potassium Salt of Lysine Solution. *Environ. Sci. Technol.* **2016**, *50* (4), 2054–2063. <https://doi.org/10.1021/acs.est.5b04515>.
- (23) Hu, G.; Smith, K. H.; Liu, L.; Kentish, S. E.; Stevens, G. W. Reaction Kinetics and Mechanism between Histidine and Carbon Dioxide. *Chem. Eng. J.* **2017**, *307*, 56–62. <https://doi.org/10.1016/j.cej.2016.08.066>.
- (24) Schimming, V.; Hoelger, C.-G.; Buntkowsky, G.; Sack, I.; Fuhrhop, J.-H.; Rocchetti, S.; Limbach, H.-H. Evidence by ¹⁵N CPMAS and ¹⁵N-¹³C REDOR NMR for Fixation of Atmospheric CO₂ by Amino Groups of Biopolymers in the Solid State. *J Am Chem Soc* **1999**, *121*, 4892–4893. <https://doi.org/10.1021/ja981747g>.
- (25) Dos, A.; Schimming, V.; Tosoni, S.; Limbach, H.-H. Acid–Base Interactions and Secondary Structures of Poly-L-Lysine Probed by ¹⁵N and ¹³C Solid State NMR and Ab Initio Model

- Calculations. *J. Phys. Chem. B* **2008**, *112*, 15604–15615. <https://doi.org/10.1021/jp806551u>.
- (26) Kaupp, G. Mechanochemistry: The Varied Applications of Mechanical Bond-Breaking. *CrystEngComm* **2009**, *11*, 388–403. <https://doi.org/10.1039/B810822F>.
- (27) James, S. L.; Adams, C. J.; Bolm, C.; Braga, D.; Collier, P.; Friščić, T.; Grepioni, F.; Harris, K. D. M.; Hyett, G.; Jones, W.; et al. Mechanochemistry: Opportunities for New and Cleaner Synthesis. *Chem Soc Rev* **2012**, *41*, 413–447. <https://doi.org/10.1039/C1CS15171A>.
- (28) Boldyreva, E. Mechanochemistry of Inorganic and Organic Systems: What Is Similar, What Is Different? *Chem. Soc. Rev.* **2013**, *42* (18), 7719–7738. <https://doi.org/10.1039/c3cs60052a>.
- (29) Friščić, T.; Mottillo, C.; Titi, H. M. Mechanochemistry for Synthesis. *Angew. Chem. Int. Ed.* **2019**. <https://doi.org/10.1002/anie.201906755>.
- (30) Beillard, A.; Bantreil, X.; Métro, T. X.; Martinez, J.; Lamaty, F. Alternative Technologies That Facilitate Access to Discrete Metal Complexes. *Chem. Rev.* **2019**. <https://doi.org/10.1021/acs.chemrev.8b00479>.
- (31) Hernández, J. G.; Bolm, C. Altering Product Selectivity by Mechanochemistry. *J. Org. Chem.* **2017**, *82* (8), 4007–4019. <https://doi.org/10.1021/acs.joc.6b02887>.
- (32) Gomollón-Bel Fernando. Ten Chemical Innovations That Will Change Our World: IUPAC Identifies Emerging Technologies in Chemistry with Potential to Make Our Planet More Sustainable. *Chem. Int.* **2019**, *41* (2), 12. <https://doi.org/10.1515/ci-2019-0203>.
- (33) Bolm, C.; Hernández, J. G. Mechanochemistry of Gaseous Reactants. *Angew. Chem. - Int. Ed.* **2019**, *58* (11), 3285–3299. <https://doi.org/10.1002/anie.201810902>.
- (34) Beillard, A.; Métro, T. X.; Bantreil, X.; Martinez, J.; Lamaty, F. Cu(0), O₂ and Mechanical Forces: A Saving Combination for Efficient Production of Cu-NHC Complexes. *Chem. Sci.* **2017**, *8* (2), 1086–1089. <https://doi.org/10.1039/c6sc03182j>.
- (35) Mori, S.; Xu, W. C.; Ishidzuki, T.; Ogasawara, N.; Imai, J.; Kobayashi, K. Mechanochemical Activation of Catalysts for CO₂ Methanation. *Appl. Catal. Gen.* **1996**, *137* (2), 255–268. [https://doi.org/10.1016/0926-860X\(95\)00319-3](https://doi.org/10.1016/0926-860X(95)00319-3).
- (36) Phung, C.; Ulrich, R. M.; Ibrahim, M.; Tighe, N. T. G.; Lieberman, D. L.; Pinhas, A. R. The Solvent-Free and Catalyst-Free Conversion of an Aziridine to an Oxazolidinone Using Only Carbon Dioxide. *Green Chem* **2011**, *13*, 3224–3229. <https://doi.org/10.1039/C1GC15850C>.
- (37) Leclaire, J.; Septavaux, J.; Métro, T.-X. Metal Extraction from Supramolecular Solids Obtained by Mechanochemistry. PCT/EP2018/074789, September 13, 2018.
- (38) Tadeppally, H. D. Chapter 8 - Recent Advances in the Industrial Production of L-Lysine by Bacteria. In *Recent Developments in Applied Microbiology and Biochemistry*; Buddolla, V., Ed.; Academic Press, 2019; pp 97–106. <https://doi.org/10.1016/B978-0-12-816328-3.00008-8>.
- (39) Williams, P. A.; Hughes, C. E.; Harris, K. D. M. L-Lysine: Exploiting Powder X-Ray Diffraction to Complete the Set of Crystal Structures of the 20 Directly Encoded

- Proteinogenic Amino Acids. *Angew. Chem. - Int. Ed.* **2015**, *54*, 3973–3977. <https://doi.org/10.1002/anie.201411520>.
- (40) Williams, P. A.; Hughes, C. E.; Martin, J.; Courvoisier, E.; Buanz, A. B. M.; Gaisford, S.; Harris, K. D. M. Understanding the Solid-State Hydration Behavior of a Common Amino Acid: Identification, Structural Characterization, and Hydration/Dehydration Processes of New Hydrate Phases of L-Lysine. *J. Phys. Chem. C* **2016**, *120*, 9385–9392. <https://doi.org/10.1021/acs.jpcc.5b12420>.
- (41) Bru, Jean. L-Lysine Carbamate. DE2951132A1, July 10, 1980.
- (42) Ciftja, A. F.; Hartono, A.; Svendsen, H. F. Carbamate Formation in Aqueous - Diamine - CO₂ Systems. *Energy Procedia* **2013**, *37* (1876), 1605–1612. <https://doi.org/10.1016/j.egypro.2013.06.036>.
- (43) Lv, B.; Jing, G.; Qian, Y.; Zhou, Z. An Efficient Absorbent of Amine-Based Amino Acid-Functionalized Ionic Liquids for CO₂ Capture: High Capacity and Regeneration Ability. *Chem. Eng. J.* **2016**, *289*, 212–218. <https://doi.org/10.1016/j.cej.2015.12.096>.
- (44) Stastny, V.; Anderson, A.; Rudkevich, D. M. Supramolecular Structures from Lysine Peptides and Carbon Dioxide. *J. Org. Chem.* **2006**, *71* (23), 8696–8705. <https://doi.org/10.1021/jo061144k>.
- (45) Frišćić, T.; Fábíán, L. Mechanochemical Conversion of a Metal Oxide into Coordination Polymers and Porous Frameworks Using Liquid-Assisted Grinding (LAG). *CrystEngComm* **2009**, *11* (5), 743. <https://doi.org/10.1039/b822934c>.
- (46) Frišćić, T.; Reid, D. G.; Halasz, I.; Stein, R. S.; Dinnebier, R. E.; Duer, M. J. Ion- and Liquid-Assisted Grinding: Improved Mechanochemical Synthesis of Metal-Organic Frameworks Reveals Salt Inclusion and Anion Templating. *Angew. Chem. - Int. Ed.* **2010**, *49* (4), 712–715. <https://doi.org/10.1002/anie.200906583>.
- (47) Bowmaker, G. A. Solvent-Assisted Mechanochemistry. *Chem Commun* **2013**, *49* (4), 334–348. <https://doi.org/10.1039/C2CC35694E>.
- (48) Hasa, D.; Miniussi, E.; Jones, W. Mechanochemical Synthesis of Multicomponent Crystals: One Liquid for One Polymorph? A Myth to Dispel. *Cryst. Growth Des.* **2016**, *16* (8), 4582–4588. <https://doi.org/10.1021/acs.cgd.6b00682>.
- (49) Al-Terkawi, A.-A.; Scholz, G.; Prinz, C.; Zimathies, A.; Emmerling, F.; Kemnitz, E. Hydrated and Dehydrated Ca-Coordination Polymers Based on Benzene-Dicarboxylates: Mechanochemical Synthesis, Structures Refinement, and Spectroscopic Characterization. *CrystEngComm* **2018**, *20*, 946–961. <https://doi.org/10.1039/C7CE01906H>.
- (50) Riss-Yaw, B.; Métro, T.-X.; Lamaty, F.; Coutrot, F. Association of Liquid-Assisted Grinding with Aging Accelerates the Inherently Slow Slipping-on of a Dibenzo-24-Crown-8 over the *N*-Hydroxysuccinimide Ester of an Ammonium-Containing Thread. *RSC Adv.* **2019**, *9* (37), 21587–21590. <https://doi.org/10.1039/C9RA05045K>.
- (51) Sheldon, R. A. The E Factor 25 Years on: The Rise of Green Chemistry and Sustainability. *Green Chem.* **2017**, *19* (1), 18–43. <https://doi.org/10.1039/C6GC02157C>.
- (52) Danckwerts, P. V. The Reaction of CO₂ with Ethanolamines. *Chem. Eng. Sci.* **1979**, *34* (4), 443–446. [https://doi.org/10.1016/0009-2509\(79\)85087-3](https://doi.org/10.1016/0009-2509(79)85087-3).

- (53) Donaldson, T. L.; Nguyen, Y. N. Carbon Dioxide Reaction Kinetics and Transport in Aqueous Amine Membranes. *Ind. Eng. Chem. Fundam.* **1980**, *19* (3), 260–266. <https://doi.org/10.1021/i160075a005>.
- (54) Crooks, J. E.; Donnellan, J. P. Kinetics and Mechanism of the Reaction between Carbon Dioxide and Amines in Aqueous Solution. *J. Chem. Soc. Perkin Trans. 2* **1989**, No. 4, 331. <https://doi.org/10.1039/p29890000331>.