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Letter

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Mechanosynthesis of Magnesium and Calcium Salt–Urea Ionic Cocrystal Fertilizer Materials for Improved Nitrogen Management

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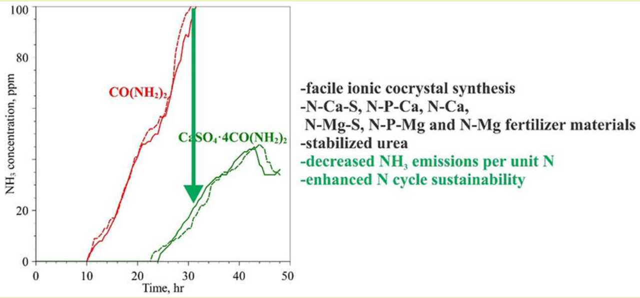
Supporting Information

ABSTRACT: Only 47% of the total fertilizer nitrogen applied to the environment is taken up by the plants whereas approximately 40% of the total fertilizer nitrogen lost to the environment reverts back into unreactive atmospheric dinitrogen that greatly affects the global nitrogen cycle including increased energy consumption for NH_3 synthesis, as well as accumulation of nitrates in drinking water. In this letter, we provide a mechanochemical method of inorganic magnesium and calcium salt–urea ionic cocrystal synthesis to obtain enhanced stability nitrogen fertilizers. The solvent-free mechanochemical synthesis presented can result in a greater manufacturing process sustainability by reducing or eliminating the need for solution handling and evaporation. NH_3 emission testing suggests that urea ionic cocrystals are capable of decreasing NH_3 emissions to the environment when compared to pure urea, thus providing implications for a sustainable global solution to the management of the nitrogen cycle.



KEYWORDS: *Fertilizers, Nitrogen, urea, Mechanochemistry, Cocrystal, pXRD, NH_3 Emissions, Stability*

INTRODUCTION

Atmospheric dinitrogen, N_2, fixation to synthesize ammonia, NH_3, consumes more than 1% of the world's primary energy.[1] It is then converted into plant absorbable nitrogen fertilizers, such as urea, $CO(NH_2)_2$. According to the International Fertilizer Association (IFA), 183 million metric tons of $CO(NH_2)_2$ were produced in 2017, and its share within all nitrogen containing fertilizers was 62%.[2] However, it has been suggested that only 47% of the applied fertilizer nitrogen is taken up by the crops[3] whereas as much as 40% of fertilizer nitrogen lost to the environment yields unreactive atmospheric N_2.[4] This is due to the inherent mismatch between the nutrient supply and plant demand,[5] which leads to nutrient loss through leaching and/or volatilization and suboptimal plant growth. Enhanced efficiency fertilizers (EEF) were designed to circumvent this and rely on (a) physical $CO(NH_2)_2$ granule coating with elemental sulfur or sulfur containing polymers, (b) $CO(NH_2)_2$ reaction products with organics, such as low solubility urea–formaldehyde or isobutylidene–urea and (c) use of urease/nitrification inhibitors.[6] The overall enhanced efficiency nitrogen fertilizer production is rather small (~3 million metric tons a year) due to their high cost as it includes natural gas derived molecules, such as aldehydes.

A conceptually interesting approach in obtaining novel EEF is the alteration of urea's reactive properties by confining it in a single molecular crystal unit with the inorganic acids or their metal salts, such as Ca or Mg phosphates, sulfates and nitrates. Reports exist where a molecular crystals of urea and phosphoric or nitric acid was shown to result only 0.7% nitrogen loss as ammonia as opposed to up to 61.1% of soil treated with urea only,[7,8] which suggests that major improvements to the global nitrogen cycle are achievable.[9,10] Additionally, urea molecular ionic cocrystals with inorganic Mg and Ca salts also contain other primary and secondary nutrients, such as P, Ca, Mg and S, which are necessary for a balanced nitrogen uptake.[11] The classical way of obtaining these crystalline Ca and Mg salt–urea ionic cocrystal materials is their precipitation from saturated aqueous solutions via heating and slow evaporation.[12,13] Mechanosynthesis, on the other hand, is a dry preparation method with plenty of opportunities in clean synthesis[14] that have already been applied in EFF engineering,[15−20] but very few compounds made were well-defined crystalline materials, such as $KMgPO_4$, NH_4MgPO_4[17] and layered double hydroxides (LDH), Mg–Al–NO_3 (Mg:Al = 3:1).[16] In addition to examples of the formation of inorganics from milling, there are numerous examples of complex organometallic structures forming from ball milling, and the technology has rapidly advanced since the beginning of the 21st century.[21] However, only one public domain literature reference exists where dry mechanochemical processing (grinding) of $CaSO_4 \cdot 2H_2O$ and $CO(NH_2)_2$ was used to obtain the $CaSO_4 \cdot 4CO(NH_2)_2$ ionic cocrystal[22] but the description of exact instrumental setup was not provided. Up to 72% conversion was achieved with the stoichiometric (1:4) reactant ratios in said experiments[22] after

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an exceptionally long 180 min milling time with an additional 80 min "induction time". It appears that the following stechnological concepts involved the use of fertilizer pulp, e.g., resorted back to solution based methods.[23,24]

In this letter, we report a cleaner, solid state transformation based synthetic procedures for producing crystalline compounds of $CaSO_4 \cdot 4CO(NH_2)_2$, $Ca(H_2PO_4)_2 \cdot 4CO(NH_2)_2$, $Ca(NO_3)_2 \cdot 4CO(NH_2)_2$, $MgSO_4 \cdot 6CO(NH_2)_2 \cdot 0.5H_2O$, $Mg(H_2PO_4)_2 \cdot 4CO(NH_2)_2$ and $Mg(NO_3)_2 \cdot 4CO(NH_2)_2 \cdot xH_2O$. The conversion of the parent materials took place to completion within 10 min of milling. Nitrogen release from urea via natural decomposition by soil enzymes to yield NH_3 is demonstrated to be significantly inhibited for $CaSO_4 \cdot 4CO(NH_2)_2$ thus providing major implications for the global nitrogen management cycle.

■ EXPERIMENTAL SECTION

Mechanochemistry and Crystal Structure Property Testing. In a typical procedure, a total of 200 mg of Ca or Mg salt and urea mixture with the corresponding molar ratios was loaded into a 15 mL stainless steel jar together with three individual 8 mm stainless steel balls and ground for 10 min at 26 Hz in a Retsch MM300 mixer mill. The crystalline nature of all reactants and products was confirmed using powder X-ray diffraction (Empyrean, PANalytical B.V.) whereas thermal stability was assessed using differential scanning calorimetry (DSC) analysis (SDT-Q600, TA Instruments). During DSC measurements, a heating rate of 10 °C/min was used under air flow of 100 mL/min. Chemicals were obtained from Sigma-Aldrich or Fischer Scientific and were of reagent or similar grade.

NH_3 Emission Testing. An ammonia testing chamber (2.32 L volume) was decontaminated with soap and water. The chamber was then placed in an oven at 80 °C to remove any moisture. The amount of silt loam soil used was 90 g and the amount of nitrogen applied as urea or $CaSO_4 \cdot 4CO(NH_2)_2$ was 0.09 g, e.g., 1 mg nitrogen (N) per 1 g of soil.[25] The amount of urea and $CaSO_4 \cdot 4CO(NH_2)_2$ used was 0.1929 and 0.3022 g, respectively, which was loaded on the surface of the soil in separate trials. NH_3 single gas detector (Gas Alert Extreme Ammonia, BW) was situated within the reaction chamber to measure NH_3 emissions over a 48 h period. The experiment was performed under static conditions in the sealed testing chamber at 23 °C and the relative humidity was 50–60%. Two sets of measurements for each urea and $CaSO_4 \cdot 4CO(NH_2)_2$ were performed to check for reproducibility.

■ RESULTS AND DISCUSSION

We considered combinations of urea with other macronutrient containing compounds, such as $CaSO_4 \cdot 2H_2O$, $Ca(H_2PO_4)_2$, $Ca(NO_3)_2 \cdot 4H_2O$, $MgSO_4 \cdot H_2O$, $Mg(H_2PO_4)_2 \cdot 2H_2O$ and $Mg(NO_3)_2 \cdot 2H_2O$. This would result in a unique single crystalline structure fertilizer material containing N–Ca–S, N–P–Ca, N–Ca, N–Mg–S, N–P–Mg and N–Mg macronutrients, respectively. As shown in Figure 1, there are very high reactant conversions near 100%. This was determined from the absence of the urea peak and the distinct new patters that resulted. A detailed comparison of every reactant, product and simulated, of the corresponding crystal structures obtained from Cambridge Crystallographic Data Centre (CCDC),[26] XRD pattern of the reported molecular crystals in the literature is provided in the Supporting Information Figure S1. It can be seen that the XRD patterns obtained match those simulated of the crystals obtained using conventional solution based routes of $CaSO_4 \cdot 4CO(NH_2)_2$,[27] $Ca(H_2PO_4)_2 \cdot 4CO(NH_2)_2$,[28] $Ca(NO_3)_2 \cdot 4CO(NH_2)_2$,[29] $MgSO_4 \cdot 6CO(NH_2)_2 \cdot 0.5H_2O$[30] and $Mg(H_2PO_4)_2 \cdot 4CO(NH_2)_2$.[28] One notable exception was $Mg(NO_3)_2 \cdot 4CO(NH_2)_2 \cdot 2H_2O$ (GEMDAF as obtained from CCDC).[31] Though the peaks in the XRD pattern below 27 degrees (2θ) match between the experimental and simulated, major peaks between 27 and 35° (2θ) do not align with theoretical representation of GEMDAF.[31] Although the powder XRD patterns are similar to the experimentally obtained and simulated of GEMDAF,[31] we note that they are not identical and an alternative crystal form materialized; therefore, the possibility of the formation of an anhydrite, hemihydrate, or monohydrate form is very likely. Further investigation will focus on the structural characterization of this new crystal phase and structure labeled in this work as $Mg(NO_3)_2 \cdot 4CO(NH_2)_2 \cdot xH_2O$.

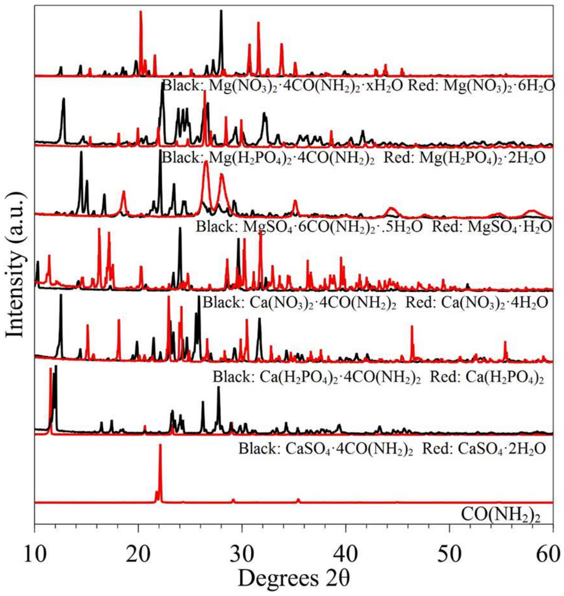

Figure 1. Powder XRD patterns of urea, magnesium or calcium salt reactants and the corresponding magnesium or calcium–urea ionic cocrystal products, e.g., $CaSO_4 \cdot 4CO(NH_2)_2$, $Ca(H_2PO_4)_2 \cdot 4CO(NH_2)_2$, $Ca(NO_3)_2 \cdot 4CO(NH_2)_2$, $MgSO_4 \cdot 6CO(NH_2)_2 \cdot 0.5H_2O$, $Mg(H_2PO_4)_2 \cdot 4CO(NH_2)_2$ and $Mg(NO_3)_2 \cdot 4CO(NH_2)_2 \cdot xH_2O$.

Other salt reactants were also considered but either did not react or resulted in new materials with unidentifiable crystal structures, such as that for $MgSO_4 \cdot 7H_2O$ derived cocrystal, as shown in Figure S1. In particular, $CaSO_4$ (anhydrous) did not produce any new compound, likely due to the absence of crystalline water as this has been observed with other organics in the pharmaceutical industry such as theophylline and citric acid.[32] This is also consistent with previous observations where conversion of $CaSO_4$ via dry milling was negligible.[22] The resulting product, $CaSO_4 \cdot 4CO(NH_2)_2$, contained no crystalline water whereas $CaSO_4 \cdot 2H_2O$ contained two. This suggests that mechanochemistry of these salts can be facilitated by crystalline water reaction. The excess of physical water added to perform liquid assisted grinding, however, did not facilitate $CaSO_4 \cdot 4CO(NH_2)_2$ formation. Further, use of $MgSO_4 \cdot 7H_2O$ resulted in a moist product which, upon drying, yielded a complex unknown crystalline pattern. This suggests that crystalline water in the reactant has a major role in the final product structure and that alternative polymorphs can be generated by selecting different precursors. This is in agreement with several compounds, especially with magnesium sulfate, where in addition to $MgSO_4 \cdot 6CO(NH_2)_2 \cdot 0.5H_2O$,[30] $MgSO_4 \cdot 6CO(NH_2)_2 \cdot H_2O$ has also been previously isolated.[33] Intermediate compounds, such as $MgSO_4 \cdot mCO(NH_2)_2 \cdot nH_2O$ and $MgSO_4 \cdot$

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xCO$(NH_2)_2 \cdot y$H$_2$O, where m and x range from 0.9 to 1.1, n ranges from 1.9 to 2.1 and y ranges from 2.9 to 3.1 and have also been isolated previously in a solid form.[34]

Differential scanning calorimetry (DSC) curves of the ionic cocrystals obtained were obtained to provide first insights into how urea is stabilized within this hybrid organic−inorganic crystal. Urea melts with an onset at 132 °C and peak value in DSC curve of 142.5 °C, as shown in Figure 2. It is generally accepted that urea thermal decomposition also commences at the same temperature even though melting is commonly reported to occur first.[35] The changes in this melting temperature can be related to the stabilization of urea within the new crystal structure as different types of bonds form. With this in mind, a series of interesting observations emerge from curves shown in Figure 2. Both metal sulfate ionic cocrystals, $MgSO_4 \cdot 6CO(NH_2)_2 \cdot 0.5H_2O$ and $CaSO_4 \cdot 4CO(NH_2)_2$, exhibit absence of the typical 132 °C peak and new melting peaks toward higher temperatures with the endothermal transition peaks at 210 °C. Metal phosphate ionic cocrystals also lack well-defined pure urea melting peaks at 132 °C with apparent new peaks at 195−197 °C although smaller peaks at 127.5 and 138 °C are apparent. These likely result from the melting of the corresponding urea phosphate fragments.[10,36] Distinct endothermal peaks are apparent at 135 and 155 °C for $Mg(NO_3)_2 \cdot 4CO(NH_2)_2 \cdot xH_2O$ and $Ca(NO_3)_2 \cdot 4CO(NH_2)_2$, respectively. The former is due to the crystalline water melting whereas the latter is due to the boiling of the resulting liquid calcium nitrate.[10] In all cases, however, absence of a strong endothermal transition with the onset at 132 °C can be observed suggesting that urea is incorporated into the new crystal structure leading to the stronger bonding.

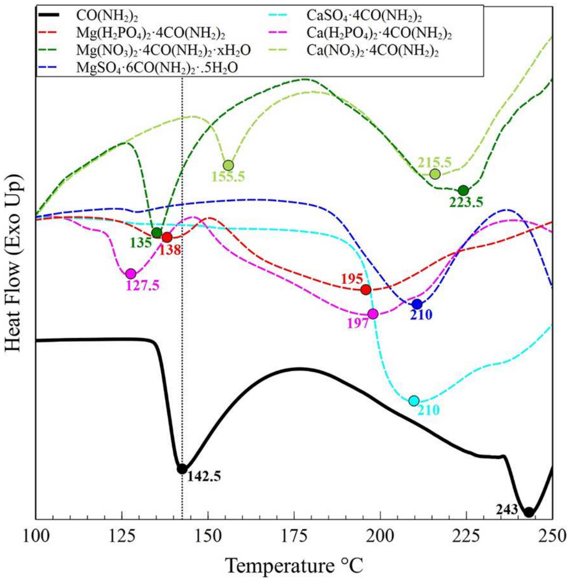

Figure 2. Differential scanning calorimetry (DSC) curves of urea and magnesium or calcium salt−urea ionic cocrystal products.

Testing of the urea and $CaSO_4 \cdot 4CO(NH_2)_2$ ionic cocrystal was performed to obtain additional insights on the stabilization of urea. This was done by dispersing either urea or $CaSO_4 \cdot 4CO(NH_2)_2$ on top of the silt loam soil used at 1 mg nitrogen (N) per 1 g of soil concentration and by monitoring NH_3 emissions in the static environment. NH_3 arises from the action of the urease enzyme resulting in significant loss of valuable plant absorbable nitrogen.[10] We hypothesized that stronger molecular bonding and secondary reactions of NH_3 within the solid ionic cocrystal with strong acid anions may decrease emissions. Measurement results are shown in Figure 3. It can be seen that NH_3 emissions from urea were linear within 30 h. $CaSO_4 \cdot 4CO(NH_2)_2$, on the other hand, resulted in remarkably decreased emissions of NH_3 peaking at 40 ppm after 42 h of the experiment. $CaSO_4 \cdot 4CO(NH_2)_2$ NH_3 emissions were delayed by 10 h when compared to urea. We hypothesize that this is due to a series of factors, including particle size difference, acid anion inhibition of urease,[37−40] decreased urea solubility due to the ionic cocrystal molecular structure, as well as the formation of secondary salts, such as $(NH_4)_2SO_4$.[9,10] Altogether, data shown in Figure 3 shows a dramatic decrease in NH_3 emissions, as much as 4-fold after 30 h, for $CaSO_4 \cdot 4CO(NH_2)_2$.

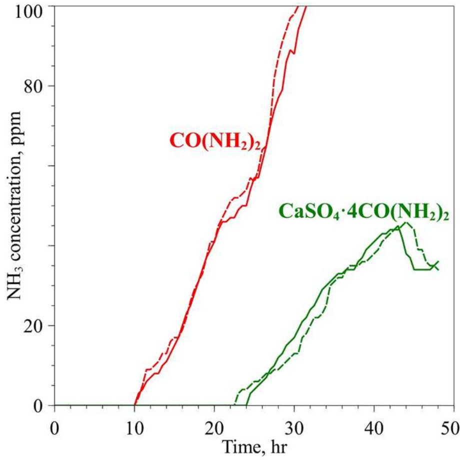

Figure 3. NH_3 emission testing from the soil containing 1 mg N/g of soil under static conditions for urea and $CaSO_4 \cdot 4CO(NH_2)_2$. Each experiment was performed and plotted twice to check for reproducibility.

CONCLUSIONS AND SUSTAINABILITY IMPLICATIONS

In this letter, we provide a mechanochemical method of magnesium and calcium salt−urea ionic cocrystal synthesis. NH_3 emission testing suggests that these ionic cocrystals are capable of decreasing nitrogen losses to the environment when compared to pure urea. To date, magnesium and calcium salt−urea ionic cocrystals chiefly have been synthesized from saturated aqueous solutions. A solvent-free mechanochemical synthesis would result in greater process sustainability by reducing or eliminating the need for solution handling and evaporation. Mechanochemical synthesis scale-up is well-known and has been addressed in many industries.[41,42] If the fertilizer industry can adopt production of these urea ionic cocrystals, reduced nitrogen losses when fertilizers are applied to soil will result. If a reactive source of solid inorganic acid and urea can be utilized, such as urea phosphates,[10] sulfates[9] and nitrates,[43] a wide variety of natural Mg and Ca bearing virtually insoluble minerals,[44] including oxides (periclase), hydroxides (brucite) and carbonates (magnesite, calcite, dolomite), can be directly transformed using this method to obtain enhanced nitrogen efficiency fertilizers. The physicochemical properties of these ionic cocrystals, such as solubility, critical to understanding the enhanced nitrogen management, are largely absent in the literature and will be the focus of the future work. Measurements to understand the interactions of these ionic cocrystals with biota that catalyzes the hydrolysis of urea into carbon dioxide and ammonia under various environmental conditions for various urea and its ionic cocrystal morphologies and particle sizes, need to be explored. Finally, interactions and stability in soil with other minerals with and without nutrients, as well as uptake of nutrients by the plants needs to be explored.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b02621.

> Powder XRD patterns of the inorganic salt and urea reactants, urea ionic cocrystal products as well as XRD patterns simulated for the urea ionic cocrystal using their available literature reported crystal structures (PDF)

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Notes

The authors declare no competing financial interest.

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