Zn(NH₃)(CO₃) Inorganic Helical Framework for Selective Separation of Carbon Dioxide

Nasser Khazeni, Reza Foudazi, Abbas Ghassemi**

Nasser Khazeni
Department of Chemical and Materials Engineering
New Mexico State University
P.O. Box 30001, MSC WERC
Las Cruces, NM 88003-8001, USA
E-mail: khazeni@nmsu.edu

Prof. Reza Foudazi
Department of Chemical and Materials Engineering
New Mexico State University
P.O. Box 30001, MSC 3805
Las Cruces, NM 88003-8001, USA

Prof. Abbas Ghassemi
Department of Chemical and Materials Engineering
New Mexico State University
P.O. Box 30001, MSC WERC
Las Cruces, NM 88003-8001, USA
E-mail: aghassem@nmsu.edu

Abstract

To explore the potential of $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ for selective CO_2 separation, this study uses single crystal X-ray diffraction and powder X-ray diffraction to determine the structure of $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ in detail; performs adsorption analyses for the compound, using N_2 , H_2 , and CO_2 as adsorbates; and, to increase the feasibility of synthesizing $\text{Zn}(\text{NH}_3)(\text{CO}_3)$, develops a single-pot synthesis approach based on urea hydrolysis and solvothermal aging. The developed single-pot synthesis method proves highly controllable, and potentially demonstrates an approach for the synthesis of other microporous structures. The $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ structure has a noteworthy inorganic helical framework that consists of a big helix of $(\text{ZnOCO})_4$ with two ammines (NH_3) pendant from every other zinc, and a small helix of $(\text{ZnOCO})_2$. In terms of adsorption capacity and CO_2 selectivity, $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ adsorbed $0.550 \text{ mmol g}^{-1} \text{ CO}_2$ at 293 K and 4500 mmHg, but only $0.047 \text{ mmol g}^{-1} \text{ N}_2$ and $0.084 \text{ mmol g}^{-1} \text{ H}_2$ at the same temperature and pressure. This behavior demonstrates considerable equilibrium selectivities – 31 and 63 – for the separation of CO_2 from H_2 and CO_2 from N_2 , respectively. During adsorption, the pendant ammines act as the gates of check-valves: applied pressure opens the gates for adsorption, and during desorption, the gates are closed, trapping the adsorbates, until a reduction of pressure to near-atmospheric levels. Therefore, low-pressure H4 hysteresis is observed, which means gas storage at near-atmospheric pressures can be done with the $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ framework. Additionally, the compound proves structurally stable, with an adsorption decrease of 0.8% after 20 adsorption/desorption cycles – a factor that, considered with the other characteristics of $\text{Zn}(\text{NH}_3)(\text{CO}_3)$, renders this compound a promising new candidate for separation of CO_2 from H_2 and N_2 .

Keywords: Single-pot Synthesis, Urea Hydrolysis, Adsorption, Selectivity, Hysteresis

1. Introduction

The environmental issues associated with CO₂ emissions have made carbon capture and storage (CCS) a major research area for materials scientists and engineers. Different materials have been explored for CCS, and some with exceptional CO₂ adsorption capacities have been synthesized. For instance, MOF-177 has been found to store 33.5 mmol g⁻¹ CO₂ at ambient temperature and 31,500 mmHg [1], and MIL-101 has been found to uptake 40 mmol g⁻¹ CO₂ at 303 K and 37,500 mmHg [2]. However, despite the synthesis of materials with such high adsorption capacities, the separation of CO₂ from other gases remains an ongoing challenge. CO₂, in the gaseous streams of the natural gas, hydrogen production, and power generation industries, typically is mixed with other gases such as N₂, CH₄, H₂, and O₂. Therefore, effective separators must have not only high storage capacities, but also high selectivities for CO₂, ideally at the operating conditions of the relevant CO₂ sources [3,4]. For instance, the flue gas of power plants is released at ambient temperature and pressure, and is composed mainly of N₂ and CO₂ at a ratio of 85:15. A representative list of materials with enhanced selectivity for CO₂ separation is presented in **Table S1** in Supplementary Information S1. In the current study, we seek to introduce a material to selectively separate CO₂ by investigating the Zn(NH₃)(CO₃) inorganic helical framework, the background of which is discussed in the following paragraphs.

Ammoniacal ammonium carbonate solution has been widely used in the leaching of metals like nickel, copper, cobalt, iron, silver, manganese, and zinc from ores [5-7]. The leaching system is usually made by a reaction between metal ore and ammonium carbonate in ammonia solution [8-

10]. Alternatively, ammonium carbamate [8] and urea [9] in water can be used; at temperatures above 363 K, ammonium and carbonate ions are released as a result of hydrolysis to form the leachant. The leaching process is based on the selective dissolution of the target metal ion from a polymetallic mixture, and therefore, in designing a suitable leaching process, it is essential to thoroughly understand the behavior of Metal-NH₃-CO₃²⁻ systems. Such an understanding allows the adoption of a set of extraction reaction parameters whose establishment results in the formation of a soluble target metal leachate from the ore without an impact to other metals, which are left in the residue.

The zinc-leaching process based on ammonium carbonate as leachant was proposed by Schnabel [10] and developed [11-13] for industrial applications. When ammoniacal ammonium carbonate (Zn-NH₃-CO₃²⁻ system) or ammonia solution (Zn-NH₃-H₂O system) is the leachant, zinc amine complex is the soluble leachate that is produced. In the Zn-NH₃-H₂O system, [Zn(NH₃)₄]²⁺ is stable in the *pH* range of 8 to 11 when the total concentration of NH₃ is 1 M [7]. Outside of this *pH* range, the stable species is zinc hydroxide. Additionally, when the concentration of ammonia increases, the stability regions of the solid phase shrink and eventually disappear [7]. The *pH* range at which zinc tetraammine complex is stable in the Zn-NH₃-CO₃²⁻ system is approximately the same for the Zn-NH₃-H₂O system [8]. It can be proposed that the extraction reaction for zinc oxide in an ammonia-ammonium carbonate system is represented by Equation (1).

Although the product of Equation (1) gives a Zn:NH₃ ratio of 1:4, reports have stated that this ratio may vary from 1:1 to 1:6, depending on the concentration of ammonia in the solution [11, 14]. Therefore, several compounds of Zn(NH₃)_x(CO₃) are possible. The compound where X=1, Zn(NH₃)(CO₃), is not soluble in water and precipitates; in the Zn-NH₃-CO₃²⁻ system, this compound is a solid phase, as is the Zn₅(OH)₆(CO₃)₂ that forms at higher zinc concentrations [8, 14,15].

On the basis of aforementioned facts, the synthesis of Zn(NH₃)(CO₃) was first reported via a two-step procedure. In this process, ammonium carbonate was reacted with either zinc oxide or zinc carbonate in an ammonia solution, forming Zn(NH₃)₄(CO₃), and then Zn(NH₃)(CO₃) was precipitated by heating, air blowing, or saturating the Zn(NH₃)₄(CO₃) solution with CO₂ at high pressure in order to lower the ammonia content of the solution [16, 17]. Initial characterization work has been performed for the produced Zn(NH₃)(CO₃), and single crystal X-ray diffraction analysis (SC-XRD) has revealed the unit cell characters of the crystalline structure. Based on the analysis, the lattice is orthorhombic with a space group of *Pna2₁* and unit cell parameters of *a* = 9.130 Å, *b* = 5.498 Å, and *c* = 7.593 Å (ICSD #41113) [18, 19].

In addition to the application of Zn(NH₃)_x(CO₃) as an intermediate in the leaching process, this compound also has been used in several other applications, including the desulfurization of catalytic reactor feeds [20] and as a filler for the adhesion retention of polymers [21].

Additionally, Zn(NH₃)(CO₃) was used as an inorganic precursor to produce zinc oxide nanoparticles by thermal decomposition in pioneering research [22]. Furthermore, the photoluminescent property of Zn(NH₃)(CO₃) at room temperature has been investigated [19].

However, with the exception of the photoluminescence study, $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ has not been used as a final product.

The main goal of this research is to use adsorption study to evaluate the selective CO_2 separation by $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ for the first time. SC-XRD, expanding on existing characterization work, is used to determine the crystalline structure of $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ in detail and interpret the adsorption properties. Since this study intends to apply $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ crystals as a separator rather than as an intermediate product, we develop a one-pot solvothermal approach to synthesize $\text{Zn}(\text{NH}_3)(\text{CO}_3)$. In this synthesis approach, zinc acetate and urea solutions in a mixture of *N,N*-dimethylformamide (DMF) and water are adopted to construct a $\text{Zn-NH}_3\text{-CO}_3^{2-}$ system that grows large, single crystals of $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ upon heating at 363 K and subsequent solvothermal aging at 423 K.

2. Experimental Section

2.1. Synthesis

$\text{Zn}(\text{NH}_3)(\text{CO}_3)$ was synthesized in a single-pot reaction through the use of urea hydrolysis and solvothermal aging. The zinc acetate dehydrate (99.9%) and urea pearls (99.99%) used in the synthesis were purchased from J. T. Baker Chemical Co., and DMF (99.8%) was obtained from Sigma-Aldrich. All chemicals were used with no further processing or purification.

In the utilized synthesis approach for $\text{Zn}(\text{NH}_3)(\text{CO}_3)$, urea (60 mg, 1 mmol) was dissolved in DMF (5 mL) in a 20-mL vial. Then, deionized water (1 mL) was slowly dripped into the urea solution in DMF and the vial was capped. The obtained solution was heated at 90-95 °C for 6 h. Afterwards, zinc acetate (329.3 mg, 1.5 mmol) was dissolved in DMF (10 mL) and dripped into

the urea solution. The mixture started to precipitate, and was heated at 90 °C for 1 h until precipitation was completed. Next, the uncapped vial of the mixture was placed into the Teflon liner of a hydrothermal reactor and heated at 150 °C for 4 days. Finally, the produced crystals were washed 3 times with DMF (10 mL), and then soaked in chloroform (10 mL) for 3 days. Every day, the used chloroform was replaced with a fresh solvent.

2.2. Structural Analysis

The structural analysis of $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ was performed using SC-XRD and PXRD studies. The SC-XRD work was performed with a Bruker SMART APEX II instrument to determine lattice parameters, crystal system, and space group. The cell parameters were compared with standard ones available in the Inorganic Crystal Structure Database (ICSD) #41113 and accessible via FindIt software. The simulated powder pattern and crystallographic information file (CIF) also could be extracted through FindIt.

The PXRD experiment was performed at room temperature with monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) using a PANalytical Empyrean X-ray diffractometer with a scan step size of 0.0033° and a 2θ scan range of $10\text{--}40^\circ$. This range covers the intense peaks of the simulated standard XRD spectrum of $\text{Zn}(\text{NH}_3)(\text{CO}_3)$.

2.3. Adsorption Analysis

The adsorption equilibrium and Brunauer, Emmett, and Teller (BET) analyses were performed with a Micromeritics™ ASAP2050 Xtended Pressure Instrument. Approximately 240 mg of $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ was used as a sample.

Before analysis, the sample was activated by heating at 110 °C under a vacuum that reduced the pressure to 10 µmHg. To check if the activation was completed, the sample was isolated and the pressure increase rate was monitored: if the rate of increase was less than 1 µmHg min⁻¹, activation was stopped. The activation process normally lasted approximately 24 h.

The adsorption isotherms were obtained at 293 K and gas pressures of up to 4500 mmHg. The temperature of the sample was controlled by circulating oil to a Dewar flask in which the sample holder was drowned. The temperature of the bath was controlled by a thermostat with a precision of ±0.01 °C.

The ASAP2050 Xtended Pressure Instrument automatically performed the dosing/vacuuming and equilibration based on the target pressure table. After initial pressure adjustment for each step, the instrument isolated the sample for equilibration. The equilibration continued until the pressure variation in the sample holder was less than 0.1% per minute. The equilibration check interval was assigned as 100 s.

3. Results and Discussion

3.1. Synthesis

Thermodynamic calculations show that zinc ammine is the dominant stable species in the Zn-NH₃-CO₃²⁻ system at *pH* 10 when concentrations of total zinc and total carbonate ions are below 0.1 M [8]. However, as the concentrations of the zinc or carbonate ions increase, the zinc ammine fraction exponentially decreases, and consequently, Zn₅(OH)₆(CO₃)₂ precipitates. Therefore, when the objective is to synthesize Zn(NH₃)(CO₃), the concentrations of zinc and carbonate sources in the reaction mixture should not exceed 0.1 M [8].

In addition to controlling the concentrations of the zinc and carbonate sources, the concentration of ammonia in the reaction mixture should be kept low enough to control the *pH* between 8 and 11 and form $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ crystals rather than soluble zinc ammine complexes. One approach to achieve this objective is to introduce ammonia to the reaction medium slowly. This can be achieved with a urea hydrolysis system. When the aqueous solution of urea is heated above 363 K, it decomposes to cyanate and ammonium ions, and consequently a series of acid/base reactions takes place. The details of the urea hydrolysis reactions are provided in Equation (S1-S11) of Supplementary Information S2. The overall effect of those reactions is a slow release of ammonia to the reaction medium, as shown in Equation (2) and (3) [23-25]:

The products of the second reaction (Equation (3)) supply the ammonia and carbonate for the $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ structure, and an ammonium ion from the first reaction (Equation (2)) serves as a buffer to maintain the *pH* in the range of 8 to 11. The overall crystal formation reaction is shown in Equation (4).

The slow release of NH_3 to the reaction medium also serves to shift the balance between nucleation and growth in the crystallization process in favor of the latter, allowing the formation

of single, large crystals. As compared to conventional processes, the developed single-pot synthesis approach allowed for much greater control over the reaction, and it provided a method that could potentially be used in the synthesis of other crystalline structures. A representative optical micrograph of a produced single crystal of $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ can be found in **Figure S1** of Supplementary Information S3.

3.2. Structural Analysis

Figure 1 shows the patterns of the produced $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ specimens as well as the simulated PXRD pattern from ICSD #41113. As can be seen, the pattern of the produced specimen is aligned with the simulated pattern for $\text{Zn}(\text{NH}_3)(\text{CO}_3)$. In addition, SC-XRD analysis performed on a single crystal sample suggested the formation of an orthorhombic lattice with $a = 9.254 \text{ \AA}$, $b = 5.416 \text{ \AA}$, $c = 7.563 \text{ \AA}$, and space group of $Pna2_1$. These results are well-congruent with reported unit cell characteristics [18, 19]. Therefore, it can be concluded that the achieved product was phase-pure $\text{Zn}(\text{NH}_3)(\text{CO}_3)$.

Figure 1. PXRD pattern from samples of produced $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ as well as a simulated pattern from the Inorganic Crystal Structure Database.

The structure of $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ is represented in **Figure 2a-d**. As revealed by SC-XRD, $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ has a helical crystalline framework, which is reproduced in **Figure 2a**. The structure consists of CO_3 trigonal planars, each of which is isolated from the others by three ZnO_3N tetrahedra that share oxygens in the corners, whereas each ZnO_3N tetrahedron keeps the N corner unshared. Regardless of polar-polar interactions between O and H and between N and H of the adjacent tetrahedra [26], the tetrahedra are also isolated from each other. With this configuration of isolated tetrahedra and trigonal planars, Zn, C, and O create two types of folded helices that develop in *b* direction (shown in orange and blue in **Figure 2a,b**): 1) a small helix of $(\text{ZnOCO})_2$, and 2) a big helix of $(\text{ZnOCO})_4$ with two ammines pendant from every other zinc toward the axis of the big helix, whose nitrogens are 4.018 Å away from each other. The helices

share the ZnOC piece of their backbones (shown in yellow in **Figure 2a,b**) and the pitches of both helices are 5.498 Å, which is equal to the *b* dimension of the Zn(NH₃)(CO₃) unit cell. The spiral direction of the helices in *c* direction stays the same, but helices are packed with a right-handed/left-handed pattern in *a* direction. The projection of the structure in *b* direction visualizes two types of microchannels with 8 and 16 components, which are shown in yellow and cyan, respectively, in **Figure 2c**.

Figure 2. (a) Crystalline structure of Zn(NH₃)(CO₃). CO₃ trigonal planars and ZnO₃N tetrahedra are shown in gray and green, respectively. The circular arrows show the spiral directions of the folded helices. The (ZnOCO)₂ and (ZnOCO)₄ helices are visualized in orange and blue, respectively. The border of the helices is shown in yellow. (b) The folded helices are shown in detail. Ammine ligands are eliminated for better visualization in this schematic. (c) Projection of crystalline structure in *b* direction. The two types of microchannels with 8 and 16 components in the Zn(NH₃)(CO₃) helical framework are shown in yellow and cyan, respectively.

3.3. Adsorption Analysis

3.3.1. Adsorption Isotherms

As can be seen from **Figure 2**, the pendant ammines in the (ZnOCO)₄ helix have enough distance between them to accommodate small gas molecules like H₂, CO₂, O₂, N₂, and CH₄, whose kinetic diameters range from 2.9 to 3.8 Å [27]. The configuration of the (ZnOCO) in helices with a pitch of 5.498 Å could make the volume of the (ZnOCO)₂ helix accessible from *a* and *c* directions for the molecules that can diffuse to the (ZnOCO)₄ helix primarily. Based upon these speculations, an adsorption property for this structure could be hypothesized.

Figure 3a-c shows the isotherms of N₂, H₂, and CO₂ uptake at 293 K. **Figure 3d** shows the adsorption branches of all of these isotherms to allow better comparison of the adsorption behavior.

The adsorption branches of the N₂ and H₂ isotherms are convex toward the pressure axis, indicating poor interaction between these nonpolar adsorbates and the microchannels of the material. The H₂ adsorption capacity of Zn(NH₃)(CO₃) at 4500 mmHg is 0.084 mmol g⁻¹, which is 1.8 times more than the N₂ capacity – 0.047 mmol g⁻¹.

The isotherm of CO₂ uptake, in contrast, is concave to the pressure axis at lower pressures and deflects toward the uptake axis (*q*) at approximately 1800 mmHg, suggesting favorable adsorbate-adsorbent interaction at lower pressures. While CO₂ has a kinetic diameter of 3.3 Å, which is larger than the diameter of H₂ (2.9 Å) and smaller than N₂ (3.6 Å) [27], the hydrogen-bond-type interaction between oxygens of CO₂ and hydrogens of pendant NH₃ [28] gives rise to

the shape of the adsorption branch of the isotherm as well as the uptake, $0.550 \text{ mmol g}^{-1}$, which is an order of magnitude higher than that of H_2 and N_2 .

Figure 3. Adsorption isotherms of $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ inorganic framework at 293 K for: (a) N_2 , (b) H_2 , and (c) CO_2 gases. Filled and open symbols represent adsorption and desorption data, respectively. (d) Adsorption branches of N_2 , H_2 , and CO_2 isotherms for comparison.

3.3.2. Selectivities

Henry's constant, which is the ratio of uptake to pressure at equilibrium and at a concentration of the adsorbate that is sufficiently low to ignore adsorbate-adsorbate interaction, provides a quantitative measure for assessing the interaction of an adsorbate with an adsorbent and to evaluate the selectivity of the synthesized material. Henry's constant can be calculated by fitting the isotherm data in a virial equation, expressed in Equation (5):

$$\frac{P}{q} = \frac{1}{K_H} \exp(C_1 q + C_2 q^2 + \dots) \quad (5)$$

in which P is pressure (kPa), q is gas uptake (mmol g⁻¹), C_1 and C_2 are virial coefficients, and K_H is Henry's constant (mmol kPa⁻¹ g⁻¹) [29, 30]. For low pressures and/or small uptakes, second and higher orders of q are small enough to be ignored. Therefore, Equation (5) can be modified as follows:

$$\ln\left(\frac{P}{q}\right) = C_1 q - \ln K_H \quad (6)$$

By performing linear regression of $\ln(P/q)$ versus q and by extrapolating the fitted line to calculate the intercept, K_H can be obtained. The calculated Henry's constants are shown in **Table 1**. The details of the calculations are also described in S4 of Supplementary Information.

Table 1. Henry's constants of N₂, H₂, and CO₂ adsorption, calculated from virial isotherm.

Adsorbate	N ₂	H ₂	CO ₂
$K_H (\text{mmol kPa}^{-1} \text{g}^{-1}) \times 10^{-4}$	0.091	0.184	5.700

Selectivity is a major characteristic for a separator, even more important than adsorption capacity. For example, selectivity is essential if the microporous material is used as a membrane for gas separation. If a separation process is designed based upon adsorption equilibrium (rather than adsorption kinetic), the selectivity of the material to separate adsorbate i from adsorbate j is defined as shown in Equation (7):

$$\alpha_{ij} = \frac{Y_i/X_i}{Y_j/X_j} \quad (7)$$

where X_i and Y_i are mole fractions of the fluid and adsorbed phases at equilibrium, respectively. If P and q are used instead of X and Y at low pressures and/or small uptakes, the selectivity can be expressed as the ratio of Henry's constants, as in Equation (8).

$$\alpha_{ij} = \frac{K_{Hi}}{K_{Hj}} \quad (8)$$

Therefore, Henry's constant, derived from the adsorption isotherm of pure gas, is an asset to assess the separation behavior of the material when it is exposed to a gas mixture. **Table 2** shows

the equilibrium separation selectivities of the material when it is exposed to the binary mixtures of N₂, H₂, and CO₂.

Table 2. Estimated selectivities for binary mixtures of N₂, H₂, and CO₂ by Zn(NH₃)(CO₃) at 293 K.

Gas Mixture	H ₂ /N ₂	CO ₂ /H ₂	CO ₂ /N ₂
α_{ij}	2.0	31.1	62.9

Regarding the similar nonpolar nature of H₂ and N₂, the preferential selectivity of H₂ over N₂ primarily follows a molecular sieving mechanism, which is based on the size exclusion principle. Note that the kinetic diameters of N₂ and H₂ are in the same scale as the micropores of the Zn(NH₃)(CO₃) helical framework. Additionally, the selectivity is approximately the same as the uptake ratio of the gases at 4500 mmHg. Therefore, the selectivity stays more or less constant in the whole range of the studied pressures. As the shapes of the adsorption isotherms of these adsorbates signify, the separation of CO₂ from H₂ and N₂ follows the thermodynamic mechanism, which is based on the differences among the interactions of the adsorbates with the walls of the material's microchannels and/or preferential adsorbate packing in the microchannels [31]. This mechanism brings about a significant selectivity to separate CO₂ from H₂, and this selectivity is intensified for CO₂ and N₂ as a result of the additional size exclusion effect.

3.3.3. Hysteresis

H4 type hysteresis [32] that extends to the origin is a common feature of the adsorbate isotherms from this study. Hysteresis associated with capillary condensation is commonly reported for mesoporous materials; in contrast, microporous materials typically show a Type I isotherm as a result of pores filling at low pressures and the levelling off of uptake at higher pressures because of limited accessible pore volume [32]. Nonetheless, hysteresis occasionally has been reported for microporous materials, and such results have been evaluated and interpreted case-by-case rather than justified by common rules like fluid or structure phase transformation [33-37].

Hysteresis is observed when the adsorption system, at least in a limited pressure range, adopts different routes in the q - P plane for gas loading than degassing. Any gas molecule to be adsorbed on the adsorption sites must be able to diffuse to these sites, and since the mass transport in microporous materials is relatively slow, adsorption on such materials is typically a diffusion-controlled process. This is the fact that can lead to hysteretic behavior in gas adsorption in microporous materials.

In the case of $\text{Zn}(\text{NH}_3)(\text{CO}_3)$, the $(\text{ZnOCO})_4$ helix (pass number 1, depicted in cyan in **Figure 4**) is the only possible channel for gas molecules to diffuse into the crystal, and it is obstructed by pendant NH_3 groups. For N_2 and H_2 molecules with relatively weak interaction with NH_3 groups to transfer to passage 1, a minimum pressure as driving force is necessary to overcome the hindrance. Upon the application of pressure and the penetration of the molecules to the $(\text{ZnOCO})_4$ helix, the volume of the $(\text{ZnOCO})_2$ helix becomes accessible with no hindering group (passage 2, illustrated in yellow in **Figure 4**). Therefore, by increasing the pressure, N_2 and H_2 uptakes by the material increase exponentially. However, the order of adsorbate release is

reversed during desorption. In other words, the gas molecules that are trapped in the $(\text{ZnOCO})_2$ helix must transfer to passage 1 to be released out of the material structure. As a result of mass transfer resistance in passage 1, desorption happens at much lower pressures, which vary depending on the kinetic diameter of the adsorbate. Therefore, it can be deduced that the NH_3 groups act as check-valves that are opened by high pressure in the adsorption process and closed in the desorption process until low pressures are reached. From all preceding information, it can be hypothesized that dual-mode, diffusion-controlled adsorption-desorption might be the origin of hysteresis adsorption behavior in $\text{Zn}(\text{NH}_3)(\text{CO}_3)$. As a quantitative measure, the approximate pressures at which 25% of the uptaken H_2 and N_2 are desorbed are 1000 and 300 mmHg, respectively.

Figure 4. a) Front view of access passes to the adsorption sites of the $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ helical framework. b) Side view of access passes to the adsorption sites of $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ helical framework. Pass numbers 1 and 2 show the direction for adsorbates to access the $(\text{ZnOCO})_4$ and $(\text{ZnOCO})_2$ helices, which are colored in cyan and yellow, respectively. The green ribbon in the side view is the area in which the projection of two helices in the ac plane direction overlaps.

For CO₂ adsorption, the favorable adsorbate-adsorbent interaction triggers the pumping of CO₂ molecules to the entrance of the (ZnOCO)₂ helices until the deflection point of the adsorption branch is reached. The uptake of CO₂, like the adsorption of N₂ and H₂, rises exponentially with increasing pressure, which facilitates penetration of the adsorbates to the inner areas of the helices. This favorable interaction has a converse function in the desorption process: because of increased mass transfer resistance, the CO₂ desorption branch, although CO₂ has a smaller kinetic diameter than N₂, ultimately behaves similarly to the N₂ desorption one. The approximate pressure at which 25% of the uptaken CO₂ is desorbed is 500 mmHg. While such hysteresis in the isotherm makes the desorption process energy demanding, it has the asset of storing gases at relatively safe pressures – that is, close to atmospheric pressure (760 mmHg). More importantly, the Zn(NH₃)(CO₃) inorganic framework can separate gas mixture through pressure difference, e.g. in a membrane separation process.

It is worthy of note that the adsorption-desorption process in microporous materials is inherently slow, and this should be considered carefully in the planning of the adsorption analysis protocol. Insufficient degassing before adsorption analysis or inadequate equilibration time during the measurement of each point will lead to artifactual hysteresis [35-38]. The common feature of the reports in which hysteresis is an artifact is that degassing or equilibration time is independently assigned in the protocol. To prevent this error, we assigned extreme criteria for degassing and equilibration, and continued equilibration and degassing until these criteria were fulfilled (see Section 2.3).

3.3.4. BET Analysis and Structural Stability

To calculate the BET surface area, N₂ adsorption analysis by Zn(NH₃)(CO₃) was performed at 77 K. **Figure 5** shows the adsorption isotherm of the material. 5.3 mmol g⁻¹ of N₂ was adsorbed at the relative pressure (P/P₀) of 0.995, where P₀ is the saturation pressure of N₂ in mmHg. The adsorption branch of the isotherm is almost linear, and hysteresis at lower pressure could still be observed.

Figure 5. N₂ adsorption isotherm at 77 K by Zn(NH₃)(CO₃), used to calculate BET surface area. Filled and open symbols represent adsorption and desorption data, respectively.

The equivalent BET surface area calculated for the Zn(NH₃)(CO₃) framework is 207 m² g⁻¹. The C-value and correlation coefficient were calculated as 2.44 and 0.9973. The C-value is a parameter used for fitting the BET equation, is exponentially related to the enthalpy of

adsorption in the first layer of adsorbed gas [39], and is a qualitative measure for adsorbate–adsorbent interaction.

The obtained BET surface area is in the range of the values reported for other microporous materials with a pore size smaller than 7 Å [33, 40, 41], known as ultramicroporous materials [42]. The details of BET analysis can be found in Supplementary Information S5.

To assess if the material is sufficiently structurally robust to withstand recurring cycles of adsorption and desorption commonly occurs in separation processes, a comparison was performed between the CO₂ adsorption isotherms of a sample of fresh Zn(NH₃)(CO₃) and Zn(NH₃)(CO₃) subjected to 20 cycles of adsorption and desorption. The maximum uptake at 4500 mmHg for the used sample was only 0.8% less than the uptake of the fresh sample, indicating that the material structure is stable under the cyclical adsorption-desorption process. In addition of structural stability, as the adsorption analysis procedure implies, Zn(NH₃)(CO₃) is thermally stable at 110 °C. To check the chemical stability to water, the crystals were mixed in water for weeks, which was found to not affect Zn(NH₃)(CO₃) structure.

4. Conclusion

A one-pot solvothermal reaction based on urea hydrolysis was developed for the first time to synthesize single crystals of the Zn(NH₃)(CO₃) inorganic helical framework. Crystallographic study revealed the existence of two types of folded helices composed of (ZnOCO)₂ and (ZnOCO)₄, with NH₃ groups inwardly pendant from either side of the bigger helix. Adsorption analysis at 293 K was performed for N₂, H₂, and CO₂. For N₂ and H₂, the Zn(NH₃)(CO₃) framework showed relatively low uptakes of 0.047 and 0.084 mmol g⁻¹, respectively, with

isotherms indicating weak adsorbate-adsorbent interactions. However, $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ adsorbed $0.550 \text{ mmol g}^{-1} \text{ CO}_2$ at 4500 mmHg, exhibiting a proper interaction of CO_2 with the microchannels of the material. This was attributed to the hydrogen-bond-type interaction between the oxygens of CO_2 and the hydrogens of the NH_3 groups pendant from the larger helix in the inorganic framework. The equilibrium selectivities for the separation of CO_2 from N_2 and H_2 were calculated as 63 and 31, respectively. All adsorption isotherms had low-pressure H4 hystereses that were assigned to the dual-mode diffusion-controlled adsorption in the microchannels of the $\text{Zn}(\text{NH}_3)(\text{CO}_3)$ helical framework. In other words, the NH_3 groups acted as check-valves that were opened by the application of high pressure in adsorption and closed, trapping the adsorbate, during the desorption process until low pressures were reached. The equivalent BET surface area for the material was measured as $207 \text{ m}^2 \text{ g}^{-1}$. The adsorption analysis also showed that the CO_2 uptake capacity of the material decreased negligibly (0.8%) after 20 adsorption–desorption cycles.

Notes

The authors declare no conflict of interest. A provisional patent application has been filed on this work.

Acknowledgements

The study was partially supported by the Office of Naval Research under award number of N00014-10-1-0711. We gratefully acknowledge Dr. Daniel Unruh from the Department of

Chemistry & Biochemistry at Texas Tech University for performing SC-XRD, and thank Patrick DeSimio at the Institute for Energy & the Environment for editing and revising the manuscript.

References

- [1] A.R. Millward, O.M. Yaghi, Metal-organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature, *Journal of the American Chemical Society* 127 (2005) 17998-17999.
- [2] P.L. Llewellyn, S. Bourrelly, C. Serre, A. Vimont, M. Daturi, L. Hamon, G. De Weireld, J.-S. Chang, D.-Y. Hong, Y. Kyu Hwang, S. Hwa Jung, G. Férey, High Uptakes of CO₂ and CH₄ in Mesoporous Metal-Organic Frameworks MIL-100 and MIL-101, *Langmuir* 24 (2008) 7245-7250.
- [3] R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O.M. Yaghi, High-throughput synthesis of zeolitic imidazolate frameworks and application to CO₂ capture, *Science* 319 (2008) 939-943.
- [4] B. Wang, A.P. Côté, H. Furukawa, M. O'Keeffe, O.M. Yaghi, Colossal cages in zeolitic imidazolate frameworks as selective carbon dioxide reservoirs, *Nature* 453 (2008) 207-211.
- [5] B.D. Pandey, V. Kumar, D. Bagchi, D.D. Akerkar, Extraction of nickel and copper from the ammoniacal leach solution of sea nodules by LIX 64N, *Industrial & Engineering Chemistry Research* 28 (1989) 1664-1669.
- [6] R.K. Jana, D.D. Akerkar, Studies of the metal-ammonia-carbon dioxide-water system in extraction metallurgy of polymetallic sea nodules, *Hydrometallurgy* 22 (1989) 363-378.

- [7] X. Meng, K.N. Han, The Principles and Applications of Ammonia Leaching of Metals-A Review, *Mineral Processing and Extractive Metallurgy Review* 16 (1996) 23-61.
- [8] L. Wang, M. Muhammed, Synthesis of zinc oxide nanoparticles with controlled morphology, *Journal of Materials Chemistry* 9 (1999) 2871-2878.
- [9] R.L. Nip, Method of Preparing Zinc Ammonia Carbonate Solution, U.S. Patent 2003/0152508 A1, August 14, 2003
- [10] C. Schnabel, Die entsilberung des werkleies durch zink und die neuesten fortschritte dieses entsilberungsmethode auf den fiskalischen hüttenwerken des Oberharzes, Ernst & Korn 1880.
- [11] T.G. Harvey, The hydrometallurgical extraction of zinc by ammonium carbonate: a review of the Schnabel process, *Mineral Processing and Extractive Metallurgy Review* 27 (2006) 231-279.
- [12] S.M. Shin, J.G. Kang, D.H. Yang, J.S. Sohn, T.H. Kim, Selective Leaching of Zinc from Spent Zinc-Carbon Battery with Ammoniacal Ammonium Carbonate, *Materials Transactions* 49 (2008) 2124-2128.
- [13] B. Kazinczy, L. Kótai, I. Gacs, K. Szentmihályi, Z. Sándor, S. Holly, Study on ammoniacal leaching of zinc from sludges containing iron and zinc hydroxides, *Hungarian Journal of Industry and Chemistry* 28 (2000) 207-210.
- [14] W. Wendt, Ammonia; ammonium carbonate leaching of low grade zinc ores, *Eng. Min. J* 154 (1953) 84-90.
- [15] G. Buckett, R. Sinclair, The BUKA Zinc Process: a 21st century standard, *Proceedings of Zinc and Lead Processing*. 1101 (1998) 579-596.

- [16] J.B. Conn, W.K. Humphrey, J.V. Magee, W.J. Wallace, Zinc oxide hyperfine: Preparation and properties, *Journal of the American Pharmaceutical Association* 45 (1956) 311-313.
- [17] J.B. Conn, Karl, Humphrey William, Process for Preparing Zinc Oxide, U. S. Patent 2,898,191, August 4, 1959
- [18] P. Besançon, S. Jaulmes, Structure et propriétés du carbonate de monoammine-zinc, *Materials Research Bulletin* 20 (1985) 1063-1067.
- [19] F. Wen, J. Chen, J.H. Kim, T. Kim, W. Li, Solvothermal Synthesis and Characterization of Zn(NH₃)CO₃ Single Crystal, *MRS Online Proceedings Library* 817 (2004) null-null.
- [20] V.S. Robinson, Process for Desulfurization Using Particulate Zinc Oxide Shapes of High Surface Area and Improved Strength, U.S. Patent 4,128,619, December 5, 1978
- [21] R.G. Parker, Highly Filled Crosslinkable Emulsion Polymer Composition U.S. Patent 4,339,370, July 13, 1982
- [22] W. Ehret, A. Greenstone, Red Zinc Oxide, *Journal of the American Chemical Society* 65 (1943) 872-877.
- [23] B. Mavis, M. Akinc, Kinetics of urea decomposition in the presence of transition metal ions: Ni²⁺, *Journal of the American Ceramic Society* 89 (2006) 471-477.
- [24] R.C. Warner, The kinetics of the hydrolysis of urea and of arginine, *Journal of Biological Chemistry* 142 (1942) 705-723.
- [25] N. Khazeni, B. Mavis, G. Gündüz, Ü. Çolak, Synthesis of zirconium tungstate-zirconia core-shell composite particles, *Materials Research Bulletin* 46 (2011) 2025-2031.
- [26] G.A. Jeffrey, *An introduction to hydrogen bonding*, Oxford university press New York 1997.
- [27] S. Kulprathipanja, *Zeolites in Industrial Separation and Catalysis*, Wiley 2010.

- [28] Y. Liu, J. Liu, M. Chang, C. Zheng, Effect of Functionalized Linker on CO₂ Binding in Zeolitic Imidazolate Frameworks: Density Functional Theory Study, *The Journal of Physical Chemistry C* 116 (2012) 16985-16991.
- [29] T.M. Letcher, *Chemical Thermodynamics for Industry*, Royal Society of Chemistry 2004.
- [30] L. Czepirski, J. JagieŁŁo, Virial-type thermal equation of gas-solid adsorption, *Chemical engineering science* 44 (1989) 797-801.
- [31] B. Crittenden, W.J. Thomas, *Adsorption Technology & Design*, Elsevier Science 1998.
- [32] M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), *Pure and Applied Chemistry* 87 (2015) 1051-1069.
- [33] L. Espinal, W. Wong-Ng, J.A. Kaduk, A.J. Allen, C.R. Snyder, C. Chiu, D.W. Siderius, L. Li, E. Cockayne, A.E. Espinal, Time-dependent CO₂ sorption hysteresis in a one-dimensional microporous octahedral molecular sieve, *Journal of the American Chemical Society* 134 (2012) 7944-7951.
- [34] C.X. Bezuidenhout, V.J. Smith, P.M. Bhatt, C. Esterhuysen, L.J. Barbour, Extreme Carbon Dioxide Sorption Hysteresis in Open-Channel Rigid Metal-Organic Frameworks, *Angewandte Chemie* 127 (2015) 2107-2111.
- [35] P.I. Ravikovitch, A.V. Neimark, Diffusion-controlled hysteresis, *Adsorption* 11 (2005) 265-270.
- [36] L. Song, Z. Sun, L. Duan, S. Jiang, L. Rees, Investigation of adsorption hysteresis in microporous materials, *Studies in Surface Science and Catalysis* 154 (2004) 1797-1803.

- [37] H.J. Choi, M. Dinca, J.R. Long, Broadly Hysteretic H₂ Adsorption in the Microporous Metal-Organic Framework Co (1, 4-benzenedipyrazolate), *Journal of the American Chemical Society* 130 (2008) 7848-7850.
- [38] A.M. Silvestre-Albero, J.M. Juárez-Galán, J. Silvestre-Albero, F. Rodríguez-Reinoso, Low-pressure hysteresis in adsorption: an artifact?, *The Journal of Physical Chemistry C* 116 (2012) 16652-16655.
- [39] D.D. Do, *Adsorption Analysis: Equilibria and Kinetics*, Imperial College Press 1998.
- [40] M. Jaroniec, M. Kruk, J.P. Olivier, Standard Nitrogen Adsorption Data for Characterization of Nanoporous Silicas, *Langmuir* 15 (1999) 5410-5413.
- [41] J.-Y. Lee, C.D. Wood, D. Bradshaw, M.J. Rosseinsky, A.I. Cooper, Hydrogen adsorption in microporous hypercrosslinked polymers, *Chemical Communications* (2006) 2670-2672.
- [42] S. Lowell, J.E. Shields, M.A. Thomas, M. Thommes, *Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density*, Springer Netherlands 2012.