

Carbon Dioxide Sensitivity of Zeolitic Imidazolate Frameworks**

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Abstract: Zeolitic imidazolate frameworks of zinc, cobalt, and cadmium, including the framework ZIF-8 commercially sold as Basolite Z1200, exhibit surprising sensitivity to carbon dioxide under mild conditions. The frameworks chemically react with CO₂ in the presence of moisture or liquid water to form carbonates. This effect, which has been previously not reported in metal–organic framework chemistry, provides an explanation for conflicting reports on ZIF-8 stability to water and is of outstanding significance for evaluating the potential applications of metal–organic frameworks, especially for CO₂ sequestration.

Zeolitic imidazolate frameworks^[1,2] (ZIFs, a family of metal azolate frameworks^[3]) have been identified as excellent candidates for applications in catalysis^[4] and gas storage and separation.^[3,5] The use of ZIFs for the sequestration, capture, and separation of CO₂ from other gases is of particular interest. The porous framework ZIF-8,^[6] based on zinc and 2-methylimidazole (HMeIm), has been studied extensively for its water stability, high storage capacity, and selectivity for CO₂ sorption, and it is now commercially manufactured as Basolite Z1200. While these properties of ZIF-8 have been validated in laboratory settings, implementation of ZIFs for CO₂ capture on an industrial scale requires a thorough understanding of stability in flue gas and in complex conditions of temperature, pressure, and atmosphere.^[7,8] Research into the stability of ZIFs to individual environmental factors determined they are stable to high temperatures, pressure, and pH.^[1,9] The CO₂ sorption capacity of ZIF-8 remains unchanged after exposure to humidity for a few days.^[10] Although the applications of ZIFs in carbon capture require a clear understanding^[11,12] of their chemical and structural resistance to water, CO₂, and other components of flue gas, different evaluations of stability of ZIF-8 towards water have recently led to conflicting results. Whereas ZIF-8 was reported to be resistant to steam for hours^[13] and stable in boiling in water for at least a week,^[1] recent reports noted the appearance of unidentified reflections in powder X-ray diffraction (PXRD) patterns of ZIF-8

after storage in room temperature water for > 24 h.^[14,15] Such apparently incongruent results highlight the need to develop reliable approaches to evaluate the long-term structural and chemical (in)stability of ZIFs. Recently, we reported the accelerated aging technique for conducting environmentally friendly synthesis of ZIFs,^[16] achieved by exposing solid reagents to high relative humidity (RH) and mild temperature (up to 45 °C) over several days, sometimes in the presence of catalytic protic salts. Besides offering a new route to make ZIF-8, accelerated aging also revealed its slow rearrangement into a non-porous polymorph with a diamondoid (*dia*) topology, *dia*-Zn(MeIm)₂.^[17]

We now demonstrate accelerated aging as a method to evaluate the long-term stability of ZIFs under different conditions of atmosphere, mild acidity, and water vapor. Importantly, we report the unexpected chemical degradation of Basolite Z1200 by humid CO₂ (Figure 1), leading to a previously not described complex carbonate (**1**). We expand this stability analysis, with similar results, to four other ZIFs based on zinc, cobalt, and cadmium involving either HMeIm or imidazole (HIm): the porous sodalite (SOD) topology Co(MeIm)₂ (ZIF-67),^[3,6] the non-porous *dia*-Zn(MeIm)₂,^[18] the non-porous interpenetrated *dia*-Cd(Im)₂,^[19] and the non-porous *zni*-Zn(Im)₂.^[20]

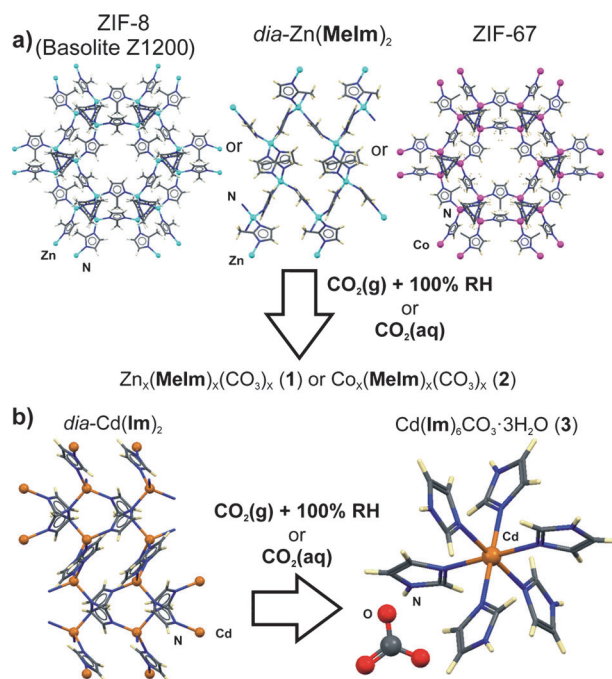


Figure 1. a) Reaction of ZIF-8, *dia*-Zn(MeIm)₂, or ZIF-67 with CO₂ in the presence of moisture leads to the formation of a carbonate phase **1** or its cobalt analogue **2**. b) Reaction of *dia*-Cd(Im)₂ with moist CO₂ yields the complex carbonate Cd(Im)₆CO₃·3 H₂O **3** (water omitted for clarity).

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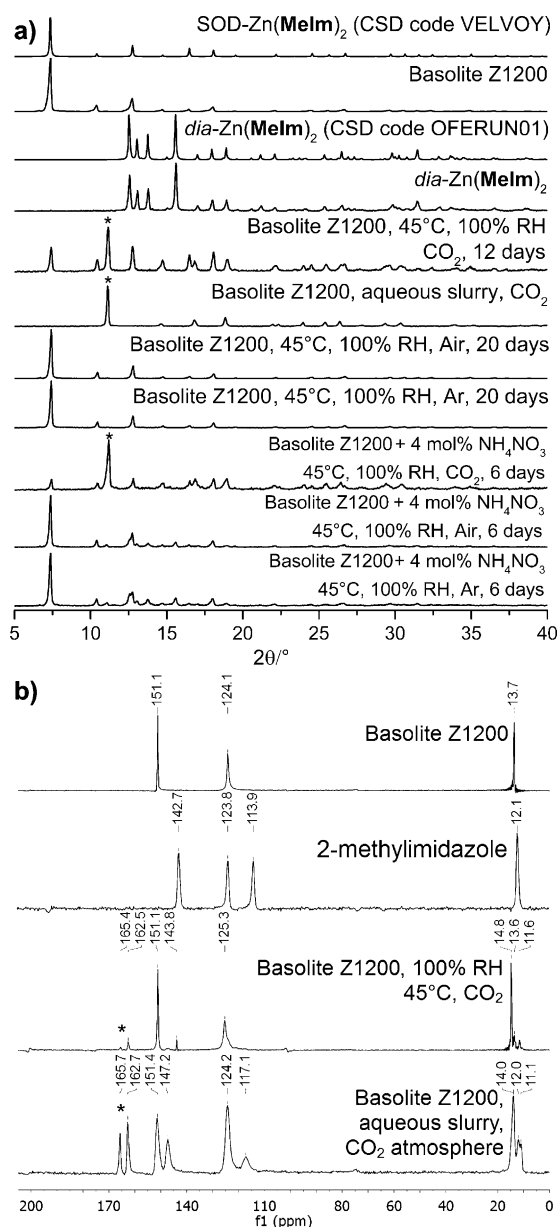


Figure 2. a) Selected PXRD patterns of aging ZIF-8 in CO₂, air, and Ar. ZIF-8 reacts with CO₂ in the presence of water and water vapor. A characteristic reflection of **1** is marked by *. b) Selected ¹³C CP-MAS SSNMR spectra for the reaction of ZIF-8 to form **1**. Signals of carbonate anions are marked with *.

Samples of Basolite Z1200 were aged at 100% RH and 45°C under air, CO₂, or Ar. After 3 days in CO₂, PXRD revealed X-ray reflections of a new crystalline phase (**1**) that could not be correlated to any reported zinc 2-methylimidazoles (Figure 2). After 12 days, PXRD indicated that the sample was a mixture of starting material and **1**. Aging of Basolite Z1200 in air and Ar did not result in any significant changes in the PXRD pattern after 20 days (Figure 2).

We next explored how protic salts affect the transformation ZIF-8 → **1**. Basolite Z1200 was mixed with 4% mol NH₄NO₃ by 5 min milling prior to aging. After 6 days, aging in moist air and Ar led to partial rearrangement of ZIF-8 into

dia-Zn(MeIm)₂ (Figure 2),^[17] while humid CO₂ gave **1**. Comparison of PXRD patterns revealed that the transformation ZIF-8 → **1** advanced more in the presence of NH₄NO₃. To verify if this might have been caused by pre-milling, pure Basolite Z1200 was milled for 5 min prior to aging in humid CO₂. In this case the reaction was slower than with NH₄NO₃, confirming that a protic additive accelerates the reaction (Supporting Information, Figure S9).

Compound **1** has, to our knowledge, not yet been explicitly described in the literature. However, inspection of the Supporting Information from a 2010 publication by Shi et al. reveals **1** in a reaction of zinc acetate and HMeIm under steam-assisted conditions.^[18] We also recognized **1** in the recently published PXRD data for ZIF-8 that was extensively washed or suspended in water,^[14,15] indicating the active participation of dissolved CO₂ in what was initially considered a hydrolytic degradation. Next, we sought a means to synthesize pure **1**. Whereas a solution reaction of Zn(NO₃)₂·6H₂O, Na₂CO₃, and HMeIm yielded a mixture of ZIF-8 and **1**, we found that **1** is readily obtained by exposing an aqueous slurry of Basolite Z1200 to CO₂ at room temperature for 2 h. The product was analyzed by thermogravimetric analysis (TGA), FTIR attenuated total reflection (FTIR-ATR), and cross-polarization magic angle spinning (CP-MAS) solid-state ¹³C NMR (SSNMR) spectroscopy. TGA in air revealed that the content of zinc in **1** is higher than in ZIF-8, indicating a loss of organic ligand in the transformation ZIF-8 → **1**. The FTIR-ATR spectrum of **1** revealed a new band at 1330 cm⁻¹, which is consistent with a carbonate (see the Supporting Information). Carbonate formation was confirmed by SSNMR, which revealed two new signals at 163.7 ppm and 165.7 ppm, consistent with two non-equivalent carbonate species (Figure 2). SSNMR also revealed the presence of at least three non-equivalent methyl groups and resolved at least two sets of signals consistent with carbon atoms of the methylimidazole ring. SSNMR of a ZIF-8 sample aged in humid CO₂ also revealed free HMeIm, confirming a higher content of zinc in **1** than in ZIF-8. The addition of 0.1M aqueous HNO₃ to **1** led to effervescence, consistent with a carbonate. Elemental analysis revealed the contents of carbon, hydrogen, and nitrogen in **1** as 33.01, 3.15, and 16.98%, respectively. These values, combined with TGA, suggest a composition Zn(MeIm)₂·ZnCO₃·0.66 HMeIm. We conclude that **1** is a complex carbonate involving carbonate and methylimidazolate species. Attempted indexing of the PXRD pattern for two different samples of **1** suggested a tentative orthorhombic unit cell with parameters $a = 24.2 \text{ \AA}$, $b = 21.3 \text{ \AA}$ and $c = 4.8 \text{ \AA}$ (see the Supporting Information).^[21]

To verify if degradation of ZIF-8 in humid CO₂ is associated with its porosity or topology, we explored the cobalt analogue of ZIF-8, SOD-Co(MeIm)₂ (ZIF-67), and the non-porous dia-Zn(MeIm)₂, zni-Zn(Im)₂ and dia-Cd(Im)₂, all readily obtained as pure bulk phases. After 9 days aging in CO₂ and 100% RH, PXRD revealed ZIF-67 formed a material (**2**) isostructural to **1** (Supporting Information, Figure S5). PXRD analysis of dia-Zn(MeIm)₂ after 1 day in CO₂ at 100% RH revealed the formation of **1** (Supporting Information, Figure S4), indicating that ZIF-8 degradation is not caused by its porosity or topology. Remarkably, zni-Zn(Im)₂

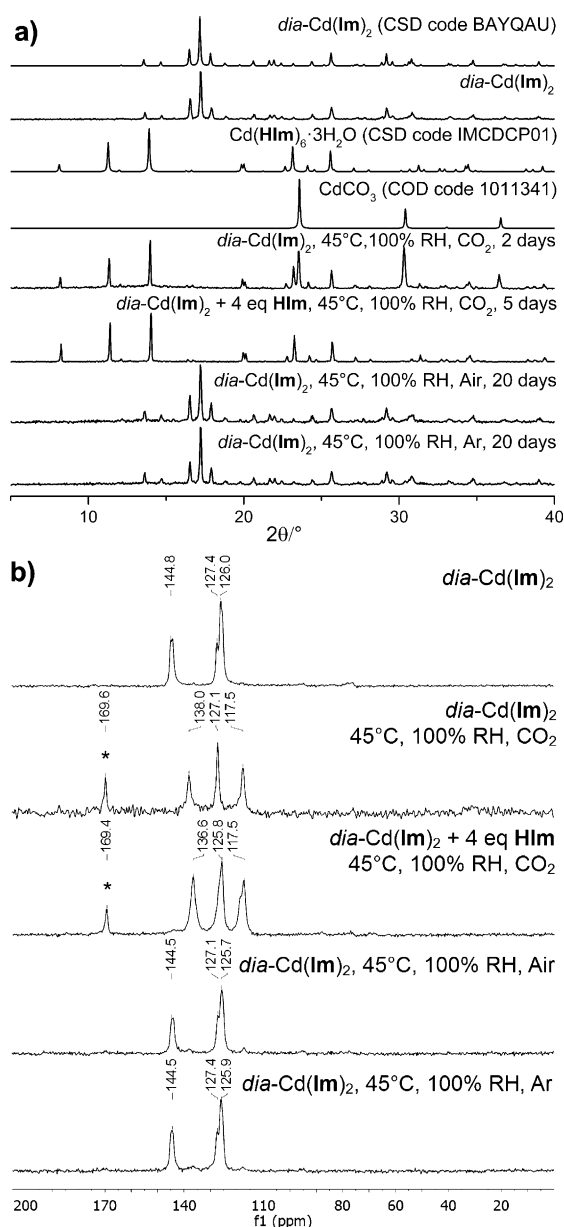


Figure 3. a) Selected PXRD patterns of aging dia-Cd(Im)_2 in CO_2 , air, and Ar. b) Selected ^{13}C CP-MAS SSNMR spectra for the reaction of dia-Cd(Im)_2 to form **3**. Signal of the carbonate anion is marked with *.

did not exhibit any sign of degradation under any of the explored conditions (Supporting Information, Figure S8).

For dia-Cd(Im)_2 ,^[19] PXRD analysis after 2 days in humid CO_2 , revealed complete disappearance of the ZIF (Figure 3). Instead, the diffractogram exhibited new reflections consistent with a mixture of cadmium carbonate (CdCO_3 , crystallography open database code 1011341) and a complex hydrated carbonate $\text{Cd(HIm)}_6\text{CO}_3 \cdot 3\text{H}_2\text{O}$ (**3**, CSD code IMCDP01), involving octahedrally coordinated Cd(HIm)_6^{2+} cations. Stirring of the product mixture in dilute (0.1M) aqueous acetic acid dissolved **3**, allowing CdCO_3 to be separated and its identity confirmed by PXRD, TGA, and FTIR-ATR. Formation of **3** and CdCO_3 results from the 1:2 ratio of Cd and HIm in the starting dia-Cd(Im)_2 . Aging of

a mixture of dia-Cd(Im)_2 and 4 equivalents of HIm (corresponding to a Cd:HIm ratio of 1:6, as in **3**) gave **3** as the only product. Exposure of dia-Cd(Im)_2 to humid air or Ar for 20 days caused no change observable by PXRD or SSNMR.

Aging of dia-Cd(Im)_2 in the presence of 4 mol % NH_4NO_3 gave similar results. In humid Ar, no change was observed. While aging in humid air demonstrated no change after 13 days, the sample converted into a mixture of the starting material, **3**, and CdCO_3 after 64 days (Supporting Information, Figure S7). Thus, even atmospheric CO_2 can cause the decomposition of certain ZIFs.

In summary, long-term exposure of ZIFs to carbon dioxide in the presence of moisture induces their chemical degradation into complex carbonates. This discovery is highly important for the development of ZIFs for carbon sequestration and, being in stark contrast to well-established stability of ZIFs in pure CO_2 , highlights the need to consider complex environments when assessing the stability of metal–organic frameworks. We have identified the complex carbonate **1** as the product of previously reported hydrolytic degradation of ZIF-8,^[14,15] indicating that the inconsistencies in evaluating ZIF-8 stability towards water might be caused by the overlooked effects of dissolved CO_2 . As the solubility of CO_2 in water drops with increasing temperature,^[22] it is possible that ZIF-8 is stable to boiling water,^[1] but slowly degrades in room temperature water that is richer in CO_2 .^[15] In support of this view, we find that the long-term exposure of different ZIFs to moisture in Ar does not lead to any noticeable changes while, in some cases, even atmospheric CO_2 in moist air caused degradation. The range of materials tested herein, including the commercial Basolite Z1200, shows that sensitivity to moist CO_2 is encountered across different framework compositions and topologies. Our study also revealed that zni-Zn(Im)_2 did not undergo any degradation, indicating that certain parameters of ZIF structure and composition can hinder their decomposition. We believe that further evaluation of long-term stability of ZIFs in multi-component environments, in combination with theoretical assessment of their stability and CO_2 binding affinity,^[5b,23] will be central for elucidating these parameters and facilitate the development of materials for CO_2 sequestration, catalytic polycarbonate synthesis, or CO_2 splitting.^[24]

Experimental Section

CO_2 stability experiments: ZIFs (1 mmol scale: 227.6 mg ZIF-8, 227.6 mg dia-Zn(MeIm)_2 , 199.6 mg zni-Zn(Im)_2 , 246.6 mg dia-Cd(Im)_2) were placed in capped vials containing an internal vial filled with distilled water as a humidity source. Vials were flushed either with air, CO_2 , or Ar and placed in an incubator at 45°C. For reactions containing NH_4NO_3 , 4 % mol (0.04 mmol, 3.2 mg) NH_4NO_3 was added to 1 mmol Basolite Z1200 or dia-Cd(Im)_2 , and the mixtures milled in a 10 mL stainless steel milling jar with one 7 mm diameter (1.3 gram) stainless steel ball for 5 min at 29.5 Hz. All reagents were purchased from Sigma–Aldrich and used without purification. A sample of ZIF-67 was provided by MOF Technologies, UK. Detailed description of ZIF syntheses and instrumental (PXRD, TGA, FTIR-ATR) characterization are given in the Supporting Information.

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