

# Supplementary Material

## Mineral neogenesis as an inspiration for mild, solvent-free synthesis of bulk microporous metal-organic frameworks from metal (Zn, Co) oxides

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## 1. EXPERIMENTAL SECTION

### 1.1 General details

Zinc oxide was calcinated in a Thermolyne furnace at 400 °C overnight prior to use in all reactions. Zinc oxide ( $\geq 99.0\%$ ), cobalt oxide (-325 mesh, 97%), imidazole (98%), 2-ethylimidazole (98%), benzimidazole (98%), and caffeine (ReagentPlus grade) were purchased from Sigma Aldrich. 2-methylimidazole (97%) was purchased from Alfa Aesar. Potassium hydrogen sulfate (Analytical reagent grade) was purchased from Mallinckrodt and potassium sulfate (ACS Reagent grade) was obtained from Anachemia. Sulfuric acid (95-98% assay) was purchased from ACP and all solvents with the exception of ethanol were obtained from Fisher. Anhydrous ethanol was purchased from Commercial Alcohols.

### 1.2 Instrumental analysis

**Powder X-ray diffraction** (PXRD) patterns were collected using a Bruker D2 Phaser powder diffractometer equipped with a Cu-K $\alpha$  ( $\lambda=1.54060$  Å) source and Lynxeye detector. The patterns were collected in the range of 4° to 40° in the case of samples containing ZnO and 4° to 50° in the case of CoO. The lower discriminial of the detector was increased from 0.110 V to 0.200 V to minimize noise resulting from x-ray fluorescence in Co-based samples. Analysis of PXRD patterns was conducted using Panalytical X'Pert Highscore Plus software.

**Fourier-transform infrared attenuated total reflectance** (FTIR-ATR) spectra were collected using a Perkin Elmer FTIR Spectrum BX spectrometer in the range 550 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>.

**Thermogravimetric analysis** (TGA) was conducted on a TA Instruments Q1000 Thermogravimetric System with a Pt pan under dynamic atmosphere of air. Samples were heated to an upper temperature limit ranging from 800°C to 900°C at a rate of 20°C/min. The balance and purge flow were 40 ml/min and 60 ml/min respectively. TGA data were used to determine the yields of the accelerated aging reactions by calcinating the well-washed and evacuated samples of synthesized frameworks up to 600 °C in air. Washing and evacuation were performed in order to remove the salt additive as well as unreacted imidazole ligand. Consequently, after washing and evacuation the samples consisted of the product framework and unreacted metal oxide ZnO or CoO. Calcination of such mixture in air leads to the oxidation of the organic framework constituents and complete conversion to either ZnO or Co<sub>3</sub>O<sub>4</sub>. The conversion of the metal oxide ( $x$ ) is calculated from the weight fraction of ZnO ( $w_{\text{ZnO}}$ ) using the equation  $x = \frac{M_{\text{ZnO}}}{w_{\text{ZnO}}(M_{\text{ZIF}} - M_{\text{ZnO}})} - \frac{M_{\text{ZnO}}}{M_{\text{ZIF}} - M_{\text{ZnO}}}$  and from the weight fraction ( $w$ ) of Co<sub>3</sub>O<sub>4</sub> using the analogous expression  $x = \frac{\frac{1}{3}M_{\text{Co}_3\text{O}_4}}{w_{\text{Co}_3\text{O}_4}(M_{\text{ZIF}} - M_{\text{CoO}})} - \frac{M_{\text{CoO}}}{M_{\text{ZIF}} - M_{\text{CoO}}}$ , where  $M_{\text{ZIF}}$  is the molecular weight of the product framework (normally ZIF-8 or ZIF-67).

**Solid-state C<sup>13</sup> and N<sup>15</sup> CP-MAS NMR** spectra were collected on a 400 MHz Varian VNMR equipped with a 7.5 mm CPMAS probe at a spin rate of 5 KHz. All N<sup>15</sup> spectra were referenced to nitromethane. All spectra were collected with a contact time of 2 ms and recycle delay of 2 s, except for that of caffeine, where the contact time was increased to 5 ms. Solution C<sup>13</sup> NMR spectra were collected in D<sub>2</sub>O on a 300 MHz Varian Mercury spectrometer equipped with a 5 mm AutoSW PFG <sup>1</sup>H/X[<sup>15</sup>N-<sup>31</sup>P] probe.

**Single crystal X-ray diffraction** data was collected on a Bruker APEX II diffractometer with  $\text{MoK}_\alpha$  ( $\lambda=0.71073 \text{ \AA}$ ) source and CCD detector. The structures were determined by least squares refinement against  $F^2$  using SHELX-97 software.

### 1.3 Synthesis of salt additives

**Caffeinium hydrogensulfate:** For the synthesis of **(Hcaf)(HSO<sub>4</sub>)** caffeine (3 mmol, 0.58 g) was dissolved in acetonitrile. Concentrated sulfuric acid (3 mmol, 160  $\mu\text{L}$ ) was added and upon stirring, a white precipitate formed. The solid was filtered and dried over vacuum. The product isolated in 90% yield was analyzed by PXRD, <sup>13</sup>C CP-MAS NMR, FTIR-ATR, and determined to be **(Hcaf)·(HSO<sub>4</sub>)** by elemental analysis. Storage in dry atmosphere was necessary to prevent conversion to **(Hcaf)·(HSO<sub>4</sub>)·H<sub>2</sub>O**, observable by PXRD. Single crystals for single crystal X-ray diffraction structure determination (Table S1) were obtained by dissolving **(Hcaf)·(HSO<sub>4</sub>)** in a 1:4 v/v solution of nitromethane and anhydrous EtOH and allowing the solvent to evaporate slowly overnight. X-ray single crystal structure determination confirmed the composition **(Hcaf)(HSO<sub>4</sub>)**, and crystallographic data has been deposited with the Crystal Structure Database. The bulk composition of the product was confirmed by comparison of powder X-ray diffraction patterns to the one simulated for the determined crystal structure. Elemental analysis for **(Hcaf)(HSO<sub>4</sub>)**: C (calculated: 32.88%, measured: 32.87%), H (calculated: 4.14%, measured: 4.14%), N (calculated: 19.17%, measured: 19.02%).

**Table S1.** General and crystallographic data for **(Hcaf)(HSO<sub>4</sub>)**

Formula	C <sub>8</sub> H <sub>12</sub> N <sub>4</sub> O <sub>6</sub> S
<i>M<sub>r</sub></i>	292.28
Crystal system	Orthorhombic
<i>a</i> /Å	6.406(1)
<i>b</i> /Å	8.167(1)
<i>c</i> /Å	23.311(4)
<i>V</i> /Å <sup>3</sup>	1219.6(3)
<i>T</i> /K	293(2)
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>Z</i>	4
Radiation type	$\text{MoK}_\alpha$
<i>μ</i> /mm <sup>-1</sup>	0.297
No. of reflections measured	13570
No. of independent reflections	2616
<i>R<sub>int</sub></i>	0.0772
<i>R<sub>I</sub></i> (for <i>I</i> > 2σ( <i>I</i> ))	0.0430
<i>wR</i> ( <i>F</i> <sup>2</sup> ) (for <i>I</i> > 2σ( <i>I</i> ))	0.0897
<i>R<sub>I</sub></i> (all data)	0.0712
<i>wR</i> ( <i>F</i> <sup>2</sup> ) (all data)	0.1006
<i>S</i>	0.955

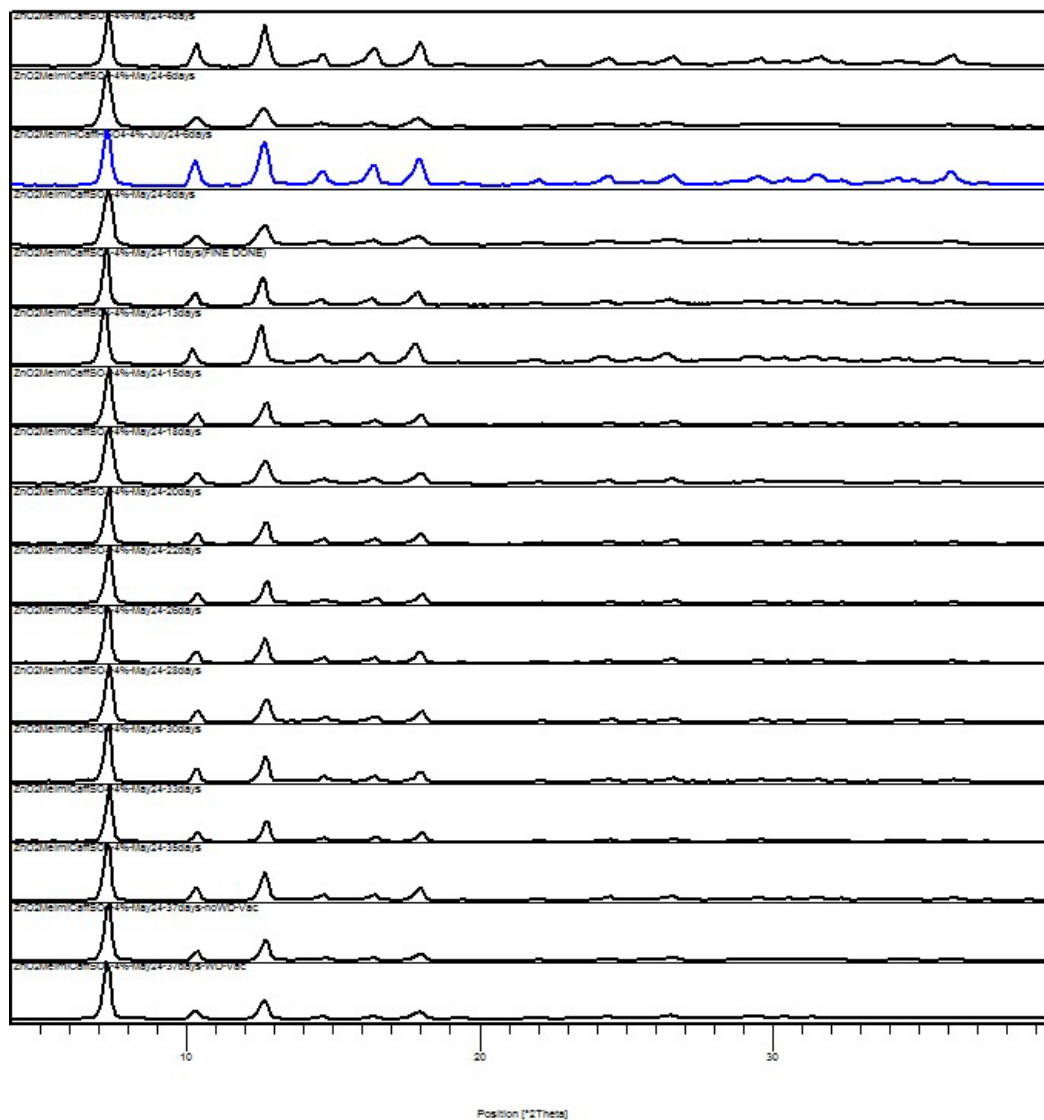
**Caffeinium hydrogensulfate hydrate:** **(Hcaf)(HSO<sub>4</sub>)** was allowed to sit in 98% RH atmosphere overnight to obtain **(Hcaf)(HSO<sub>4</sub>)·H<sub>2</sub>O**. The product was analyzed by FTIR-ATR spectroscopy, PXRD and TGA. Powder X-ray diffraction pattern matched to that simulated from the known crystal structure (see Jerin, Athimoolam, *Acta Crystallogr.* **2011**, E67, o2290); **Benzimidazolium sulfate:** Benzimidazole (8 mmol, 0.55 g) was dissolved in acetonitrile. Concentrated sulfuric acid (8 mmol, 520  $\mu\text{L}$ ) was added to form a beige precipitate. The product was collected, dried over vacuum to obtain 97% isolated yield, and characterized by PXRD and FTIR-ATR spectroscopy. **Imidazolium Sulfate Dihydrate:** Imidazole (4 mmol, 0.272 g) was dissolved in a 1:9 water:ethanol (v/v) mixture. Concentrated sulfuric acid (2.1 mmol, 111  $\mu\text{L}$ ) was added and a white precipitate formed. The

product was collected over vacuum and dried over air (96% isolated yield). Elemental analysis for  $(\mathbf{H_2Im})_2(\text{SO}_4) \cdot 2\text{H}_2\text{O}$ : C (calculated: 26.67%, measured: 26.41%), H (calculated: 5.22%; measured: 5.54%), N (calculated: 20.73%, measured: 20.38%).

#### 1.4 Accelerated aging

In a typical experiment, 2 mmol of metal oxide (ZnO or CoO), 4 mmol of the imidazole ligand ( $\mathbf{HMeIm}$  or  $\mathbf{HEtIm}$ ), and 4 mol% (unless otherwise specified) of the salt additive [ $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{KHSO}_4$ ,  $(\mathbf{H_2Im})_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ,  $(\mathbf{Hcaf})(\text{HSO}_4)$ ,  $(\mathbf{Hcaf})(\text{HSO}_4) \cdot \text{H}_2\text{O}$ , or  $(\mathbf{H_2BIm})_2(\text{SO}_4)$ , percentage calculated with respect to ZnO] were added to a 10 mL stainless steel milling jar along with one stainless steel ball of 7 mm diameter. Unless specified otherwise, the mixtures were briefly milled using a Retsch MM400 ball mill for 5 minutes at 29.5 Hz. The samples not containing ammonium salt were left to age in a Secador controlled humidity chamber at 98% RH or nominal 100% RH, which was situated in an incubator set at 45°C. Samples containing ammonium sulfate as the additive were placed in a separate controlled humidity glass chambers under the same conditions, so as to avoid possible absorption of  $\text{NH}_3$  within the container walls and contamination of subsequent samples. Saturated  $\text{K}_2\text{SO}_4$  solution (for 98% RH) or just water (for nominal 100% RH) were used to maintain humid atmosphere. Upon complete disappearance of X-reflections representing the metal oxides in PXRD patterns, samples were washed overnight and filtered over vacuum in  $\text{H}_2\text{O}$ , MeOH, or acetonitrile to remove trace amounts of catalyst or organic ligand. Samples for gas adsorption analysis were evacuated in a vacuum oven at 80 °C overnight.

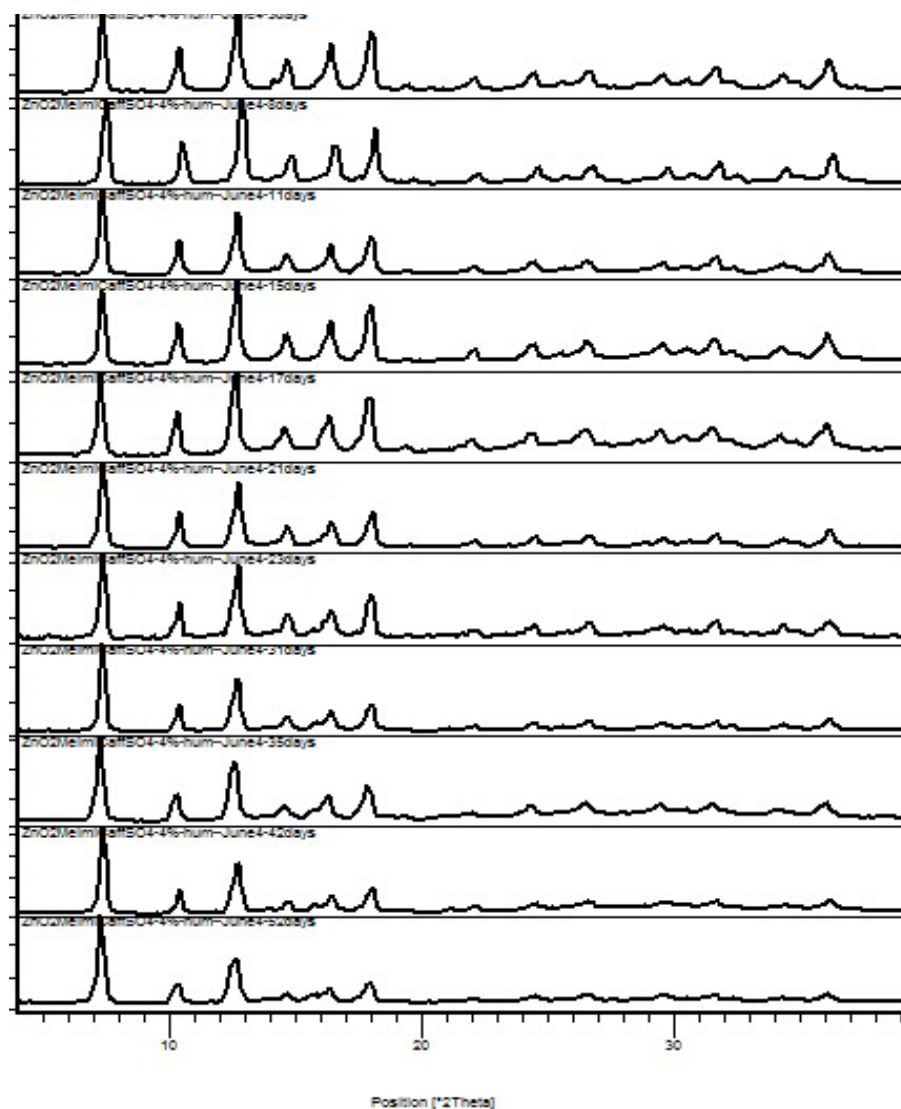
## 2. SELECTED POWDER X-RAY DIFFRACTION (PXRD) PATTERNS



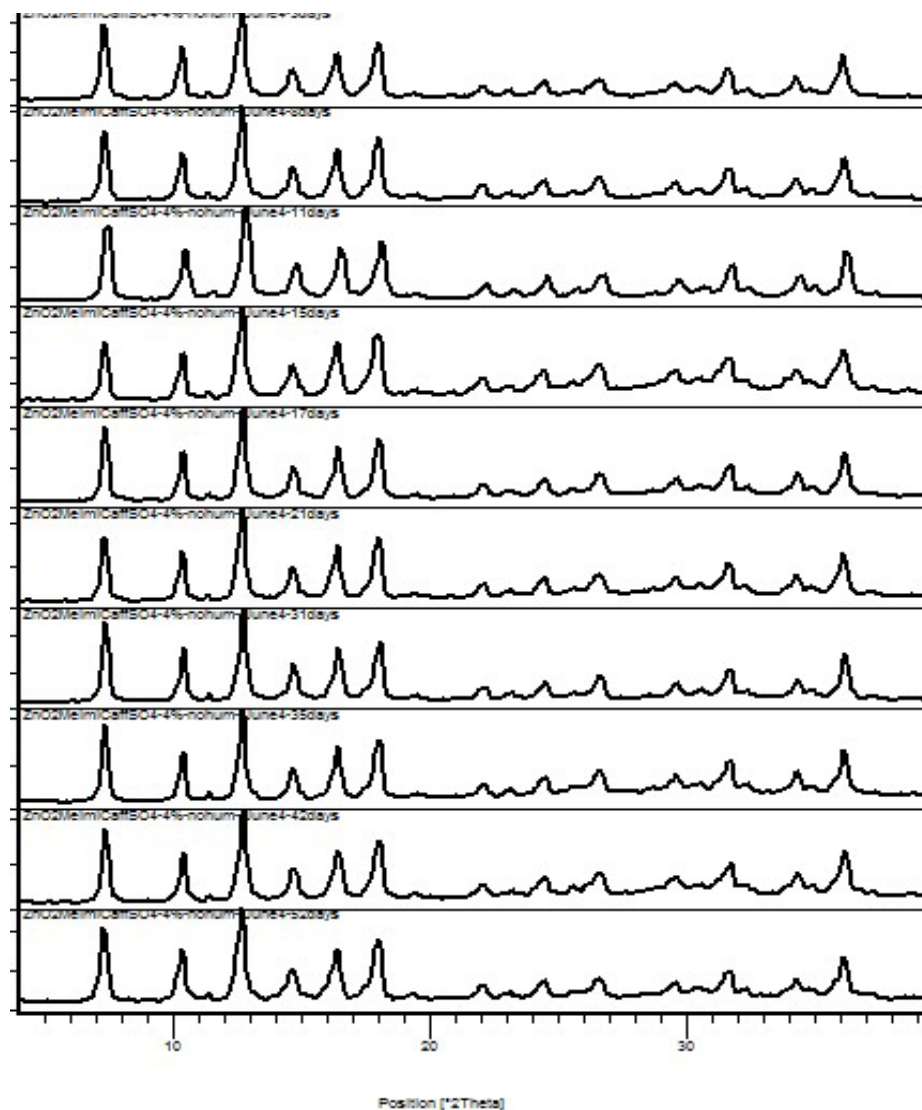
**Figure S1.** Powder X-ray diffraction patterns for the accelerated aging reaction of **HMeIm** and ZnO, with **(Hcaf)(HSO<sub>4</sub>)** as the ionic additive (from top to bottom), at 45 °C and 98% RH: 4 days aging; 6 days aging; the sample obtained after 6 days aging with **(Hcaf)(HSO<sub>4</sub>)·H<sub>2</sub>O** (blue) shown for comparison with the previous sample; 8 days aging; 11 days aging; 13 days aging; 15 days aging; 18 days aging; 20 days aging; 22 days aging; 26 days aging; 28 days aging; 30 days aging; 33 days aging; 35 days aging; evacuated sample after 37 days aging and washed (acetonitrile?) and evacuated sample after 37 days aging.

The comparison of the PXRD pattern for the sample obtained after 6 days aging with 4 mol% **(Hcaf)(HSO<sub>4</sub>)·H<sub>2</sub>O** (shown in blue) with the sample obtained after 6 days aging with 4mol% **(Hcaf)(HSO<sub>4</sub>)** clearly demonstrates a larger amount of ZnO present with the hydrated salt as the additive.



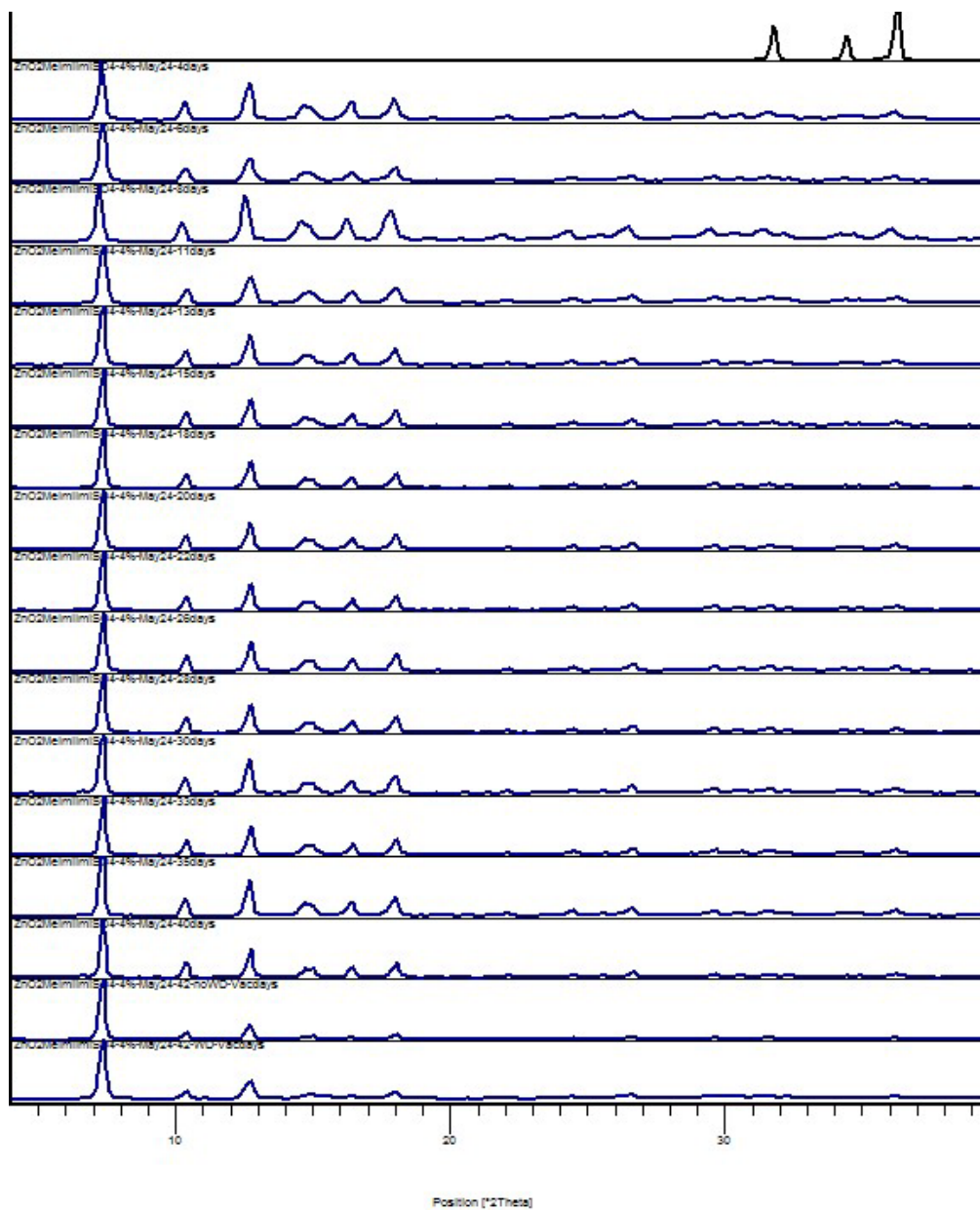


**Figure S2.** Powder X-ray diffraction patterns for the accelerated aging reaction of **HMeIm** and ZnO, with **(Hcaf)(HSO<sub>4</sub>)** as the ionic additive (from top to bottom), at 98% RH and room temperature: 3 days aging; 8 days aging; 11 days aging; 15 days aging; 17 days aging; 21 days aging; 23 days aging; 31 days aging; 35 days aging; 42 days aging; 52 days aging.

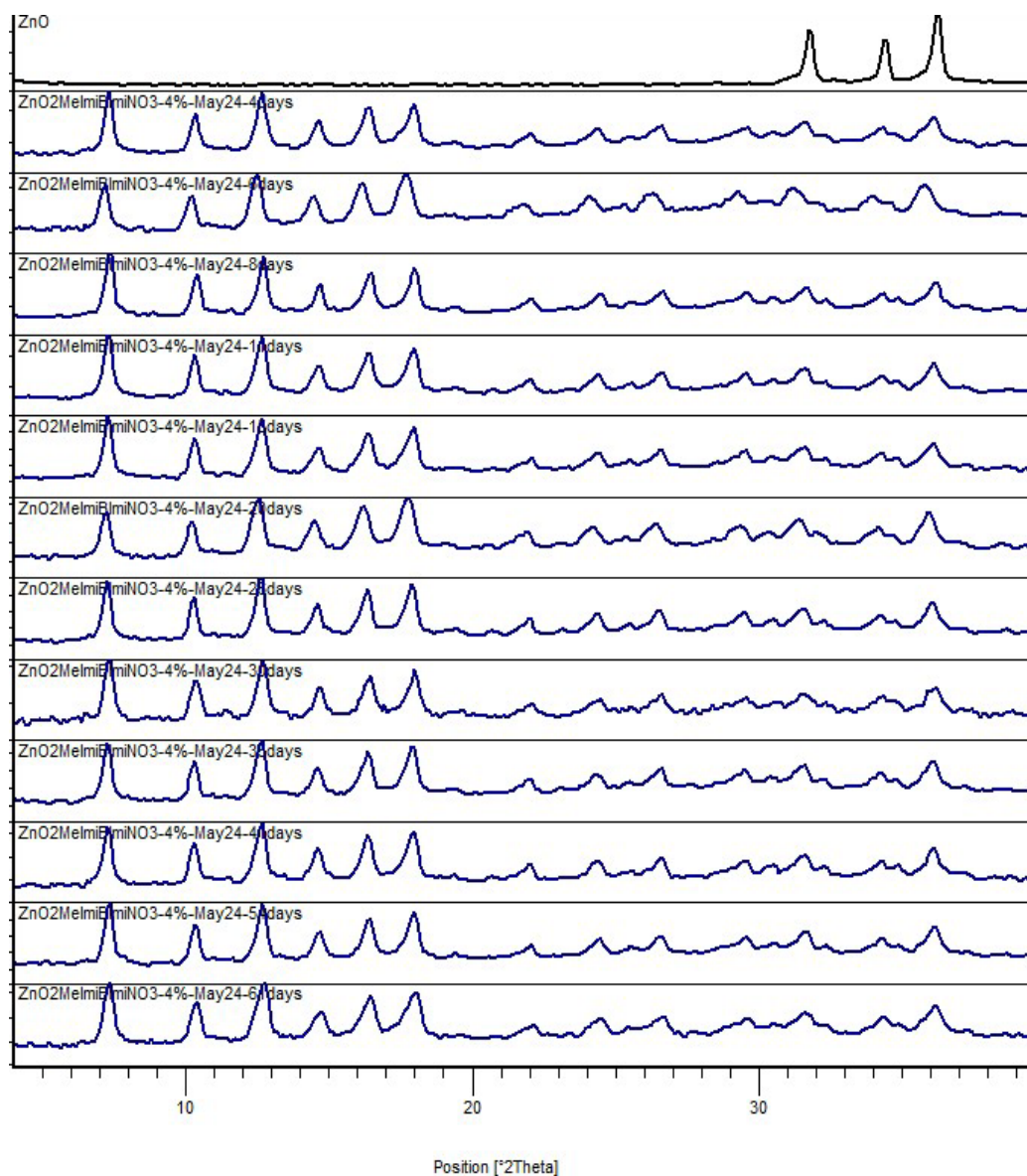


**Figure S3.** Powder X-ray diffraction patterns for the accelerated aging reaction of **HMeIm** and ZnO, with **(Hcaf)(HSO<sub>4</sub>)** as the ionic additive (from top to bottom), at room temperature and humidity: 3 days aging; 8 days aging; 11 days aging; 15 days aging; 17 days aging; 21 days aging; 31 days aging; 35 days aging; 42 days aging; 52 days aging.

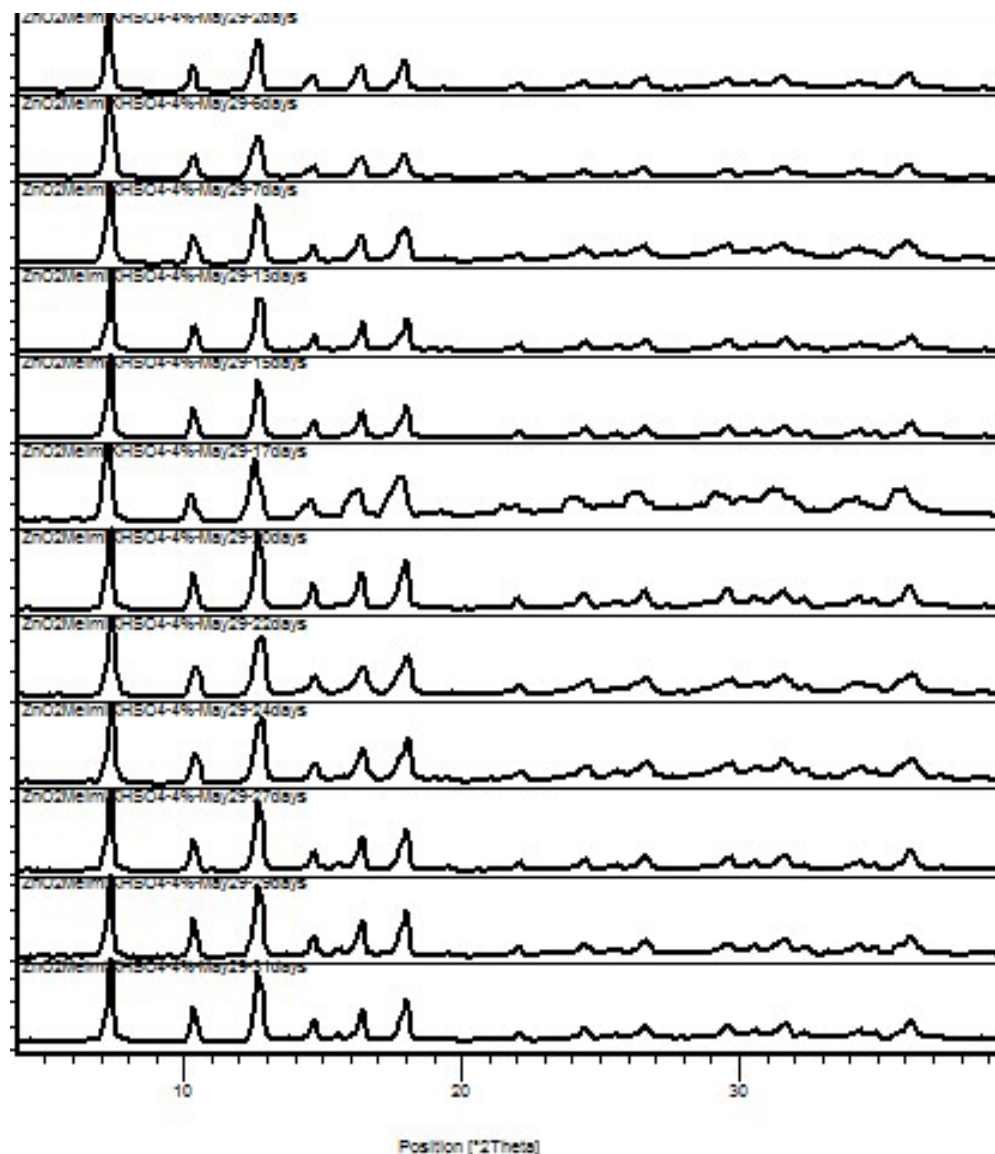




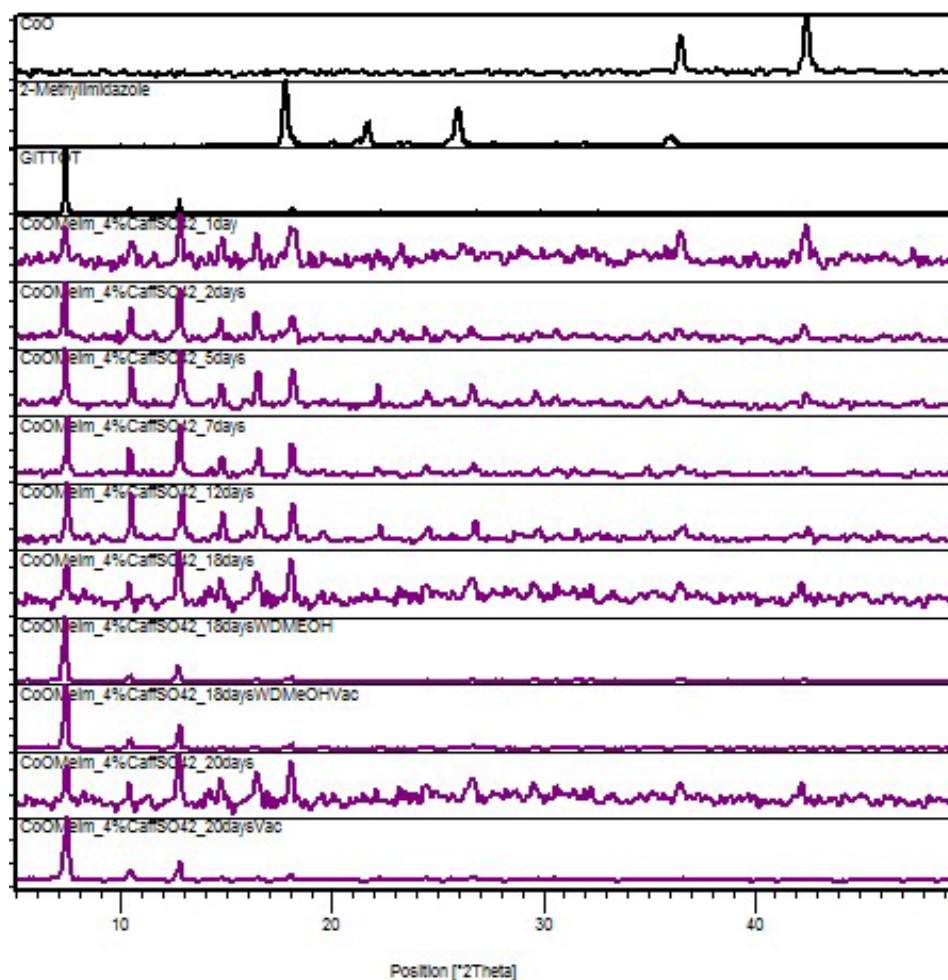
**Figure S4.** Powder X-ray diffraction patterns for the accelerated aging reaction of **HMeIm** and ZnO, with  $(\text{H}_2\text{Im})_2(\text{SO}_4) \cdot 2\text{H}_2\text{O}$  as the ionic additive (from top to bottom), at 45 °C and 98% RH: ZnO reactant; sample after 4 days aging; 6 days aging; 8 days aging; 11 days aging; 13 days aging; 15 days aging; 18 days aging; 20 days aging; 22 days aging; 26 days aging; 28 days aging; 30 days aging; 33 days aging; 35 days aging; 40 days aging; sample after 40 days aging and evacuation; sample after 40 days aging, washing with methanol and evacuation.



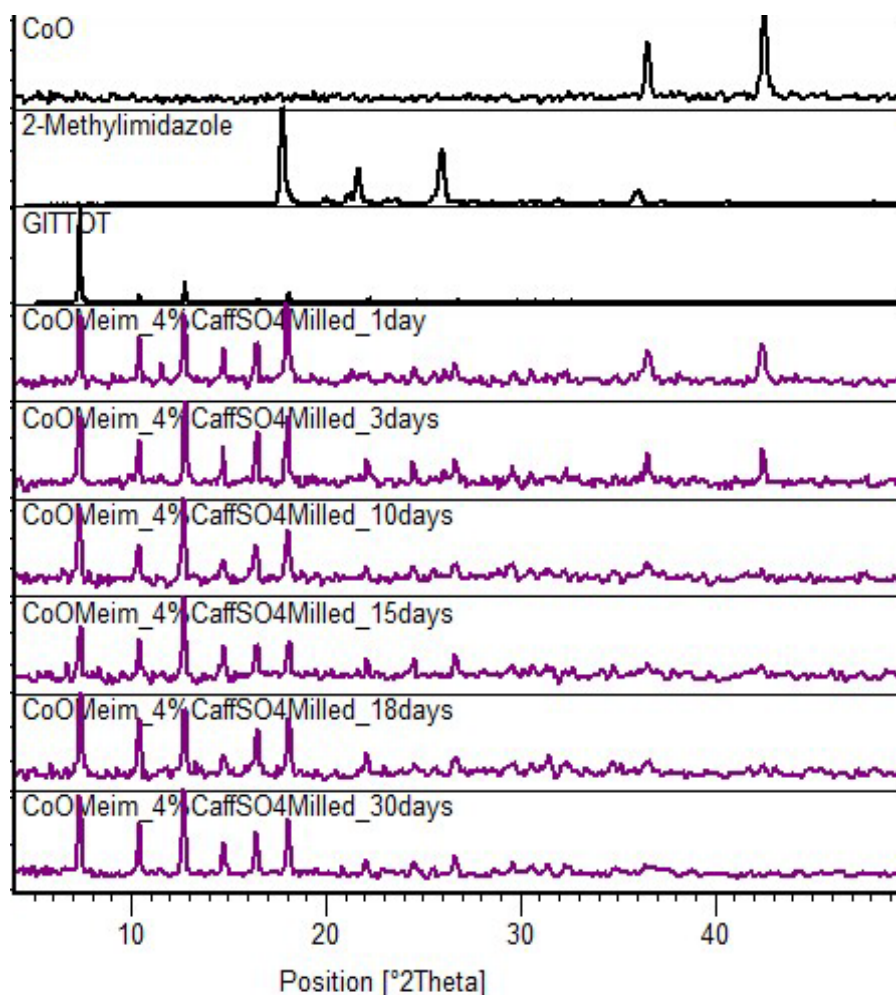
**Figure S5.** Powder X-ray diffraction patterns for the accelerated aging reaction of **HMeIm** and ZnO, with **(H<sub>2</sub>BIm)<sub>2</sub>SO<sub>4</sub>** as the ionic additive (from top to bottom), at 45 °C and 98% RH: ZnO reactant; sample after 4 days aging; 6 days aging; 8 days aging; 11 days aging; 13 days aging; 20 days aging; 26 days aging; 30 days aging; 35 days aging; 41 days aging; 54 days aging and after 61 day aging.



**Figure S6.** Powder X-ray diffraction patterns for the accelerated aging reaction of **HMeIm** and ZnO, with KHSO<sub>4</sub> as the ionic additive (from top to bottom), at 45 °C and 98% RH: 2 days aging; 6 days aging; 7 days aging; 13 days aging; 15 days aging; 17 days aging; 20 days aging; 22 days aging; 24 days aging; 27 days aging; 29 days aging; 31 days aging.

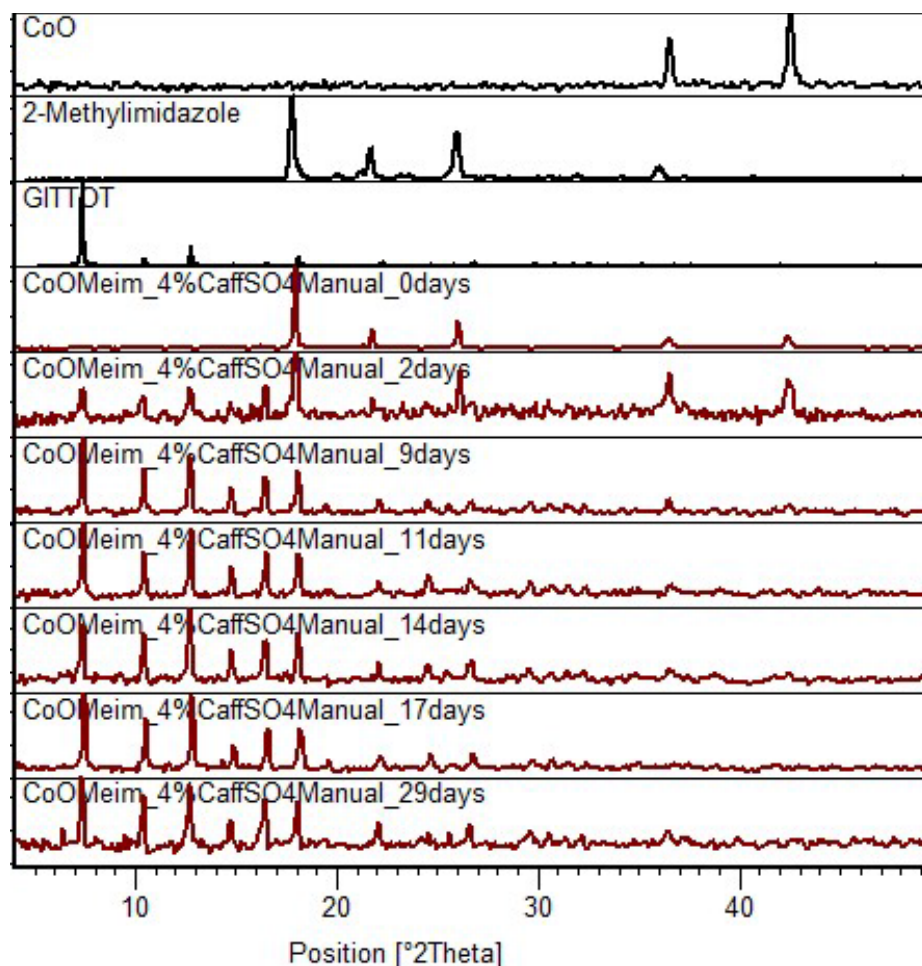


**Figure S7.** Powder X-ray diffraction patterns for the accelerated aging reaction of **HMeIm** and CoO, with (**Hcaf**)(HSO<sub>4</sub>) (4 mol% with respect to CoO) as the ionic additive at 45 °C and 98% RH (from top to bottom): CoO reactant, **HMeIm** reactant; calculated pattern for ZIF-67 (CCDC code GITTOT); 1 day aging; 2 days aging; 5 days aging; 7 days aging; 12 days aging; 18 days aging; sample after 18 days aging after washing with methanol; sample after 18 days aging after washing with methanol and evacuation; sample after 20 days aging; sample after 20 days aging after evacuation.



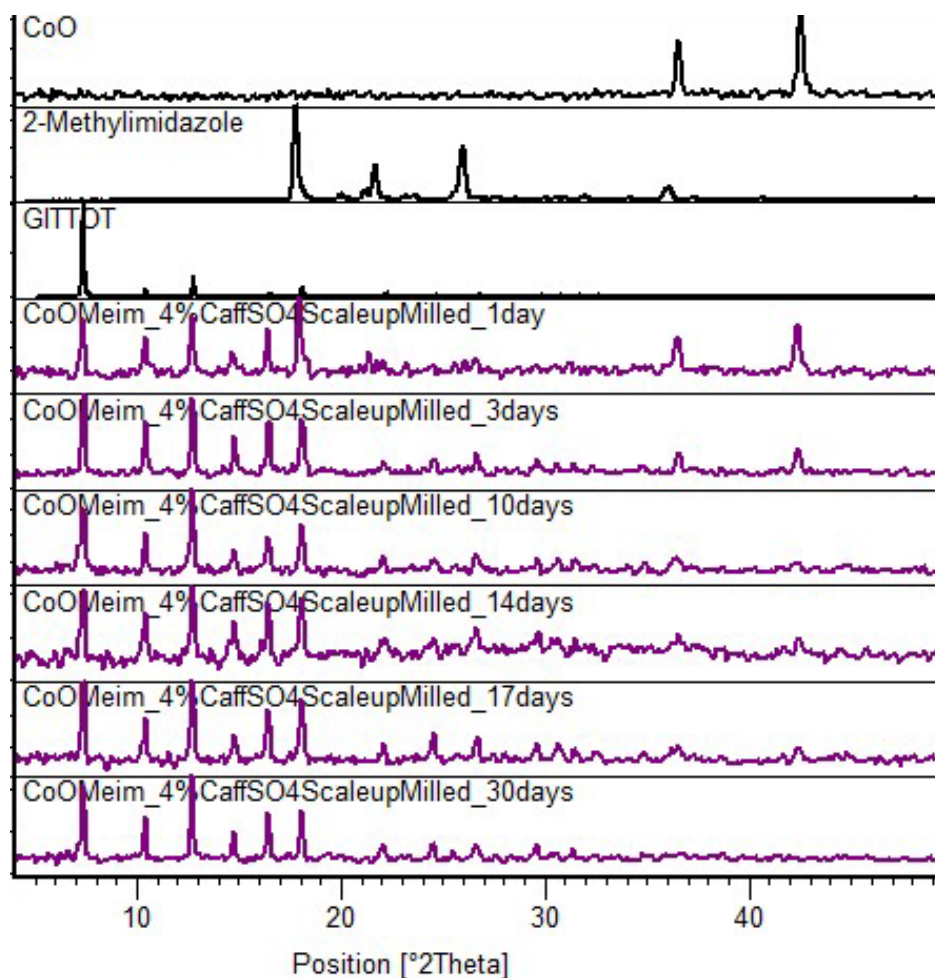
**Figure S8.** Powder X-ray diffraction patterns for the repeated accelerated aging reaction of **HMeIm** and CoO, with (**Hcaf**)(HSO<sub>4</sub>) (4 mol% with respect to CoO) as the ionic additive at 45 °C and 98% RH (from top to bottom): CoO reactant, **HMeIm** reactant; calculated pattern for ZIF-67 (CSD code GITTOT); 1 day aging; 3 days aging; 10 days aging; 15 days aging; 18 days aging and 30 days aging.



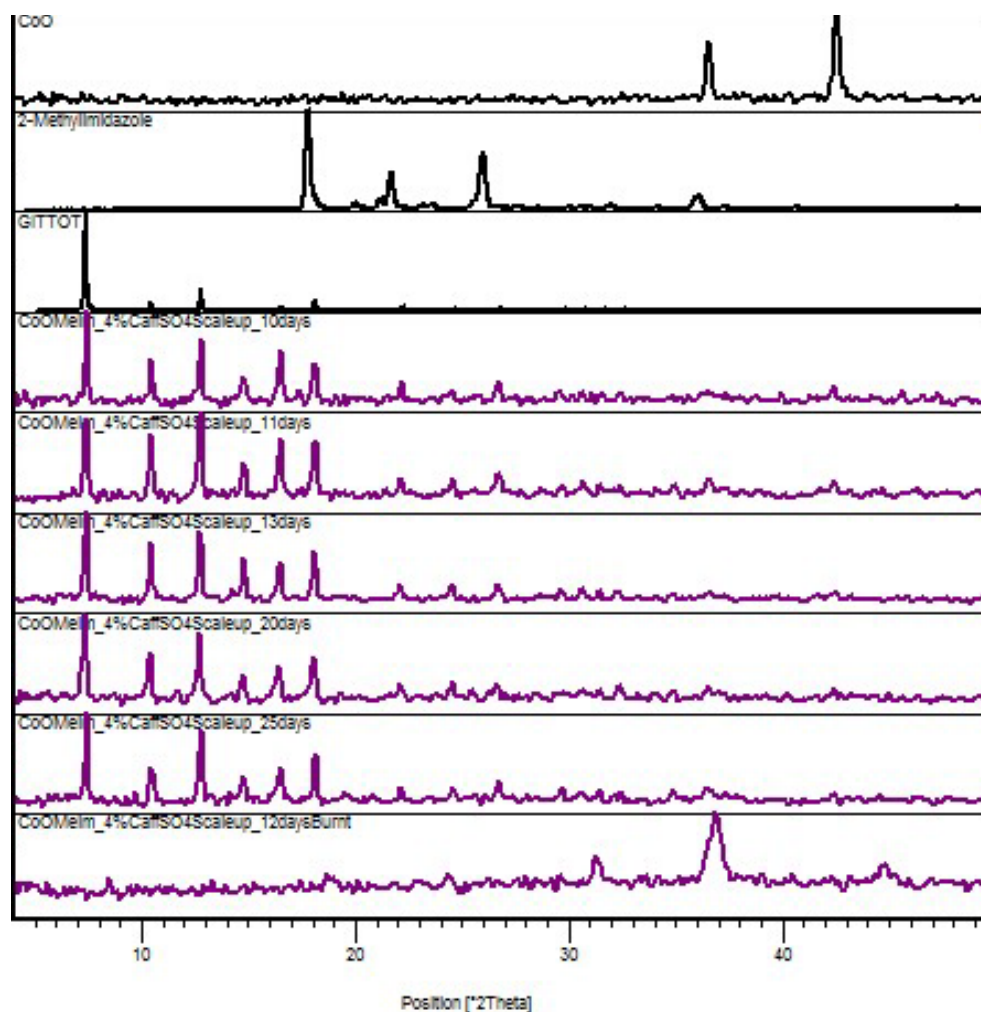


**Figure S9.** Powder X-ray diffraction patterns for the repeated accelerated aging reaction of **HMeIm** and CoO, with (**Hcaf**)(HSO<sub>4</sub>) (4 mol% with respect to CoO) as the ionic additive. The reaction mixture was prepared by manual mixing in a mortar and pestle, in order to investigate the potential role of mechanical activation in other samples prepared by milling. The accelerated aging was conducted at 45 °C and 98% RH (from top to bottom): CoO reactant, **HMeIm** reactant; calculated pattern for ZIF-67 (CSD code GITTOT); reaction mixture immediately after mixing; 2 days aging; 9 days aging; 11 days aging; 14 days aging; 17 days aging and 29 days aging.

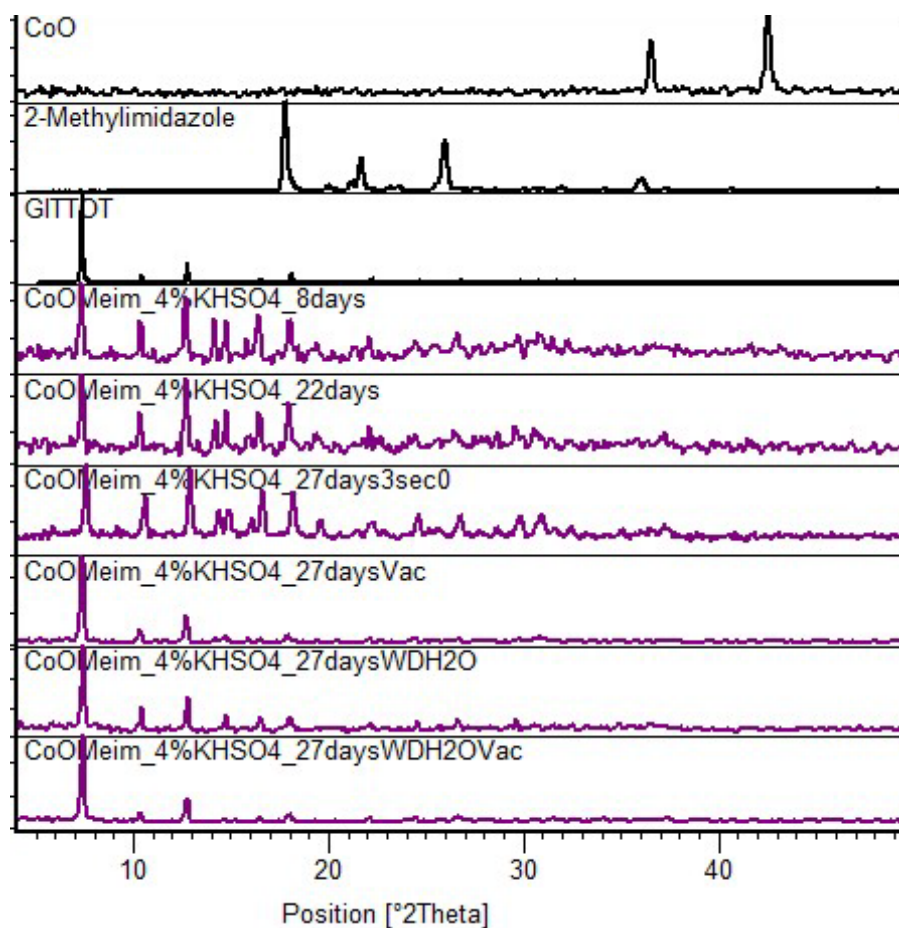




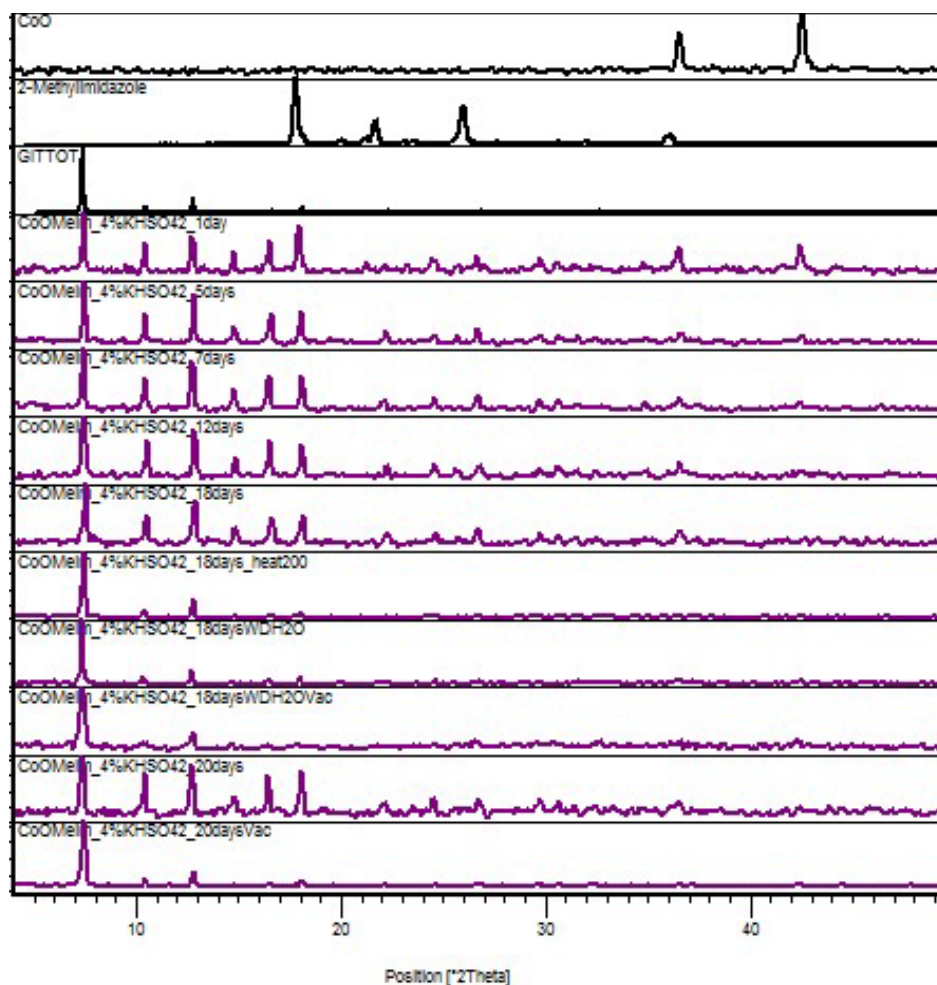
**Figure S10.** Powder X-ray diffraction patterns for the 5-gram scale accelerated aging reaction of **HMeIm** and CoO, with (**Hcaf**)(HSO<sub>4</sub>) (4 mol% with respect to CoO) as the ionic additive. The reaction mixture was prepared by manual mixing of reactants and the catalytic salt in a mortar and pestle. The accelerated aging was conducted at 45 °C and 98% RH (from top to bottom): CoO reactant, **HMeIm** reactant; calculated pattern for ZIF-67 (CSD code GITTOT); reaction mixture after 1 day aging; 3 days aging; 10 days aging; 14 days aging; 17 days aging and 30 days aging.



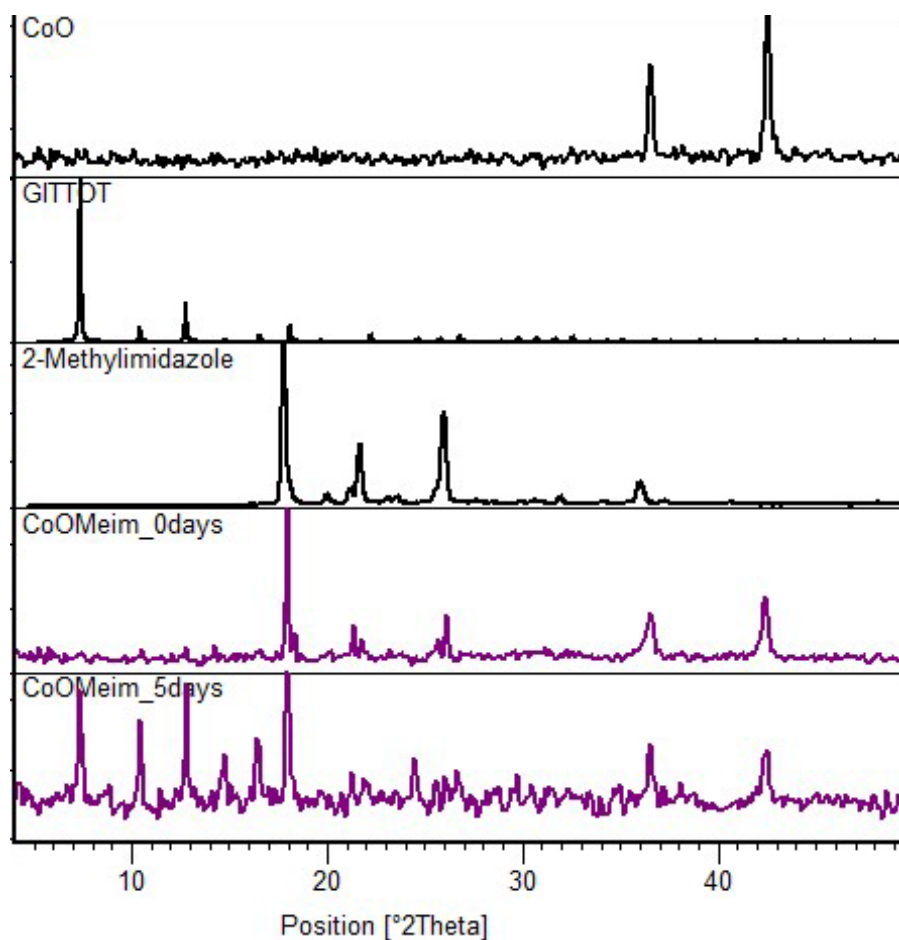
**Figure S11.** Powder X-ray diffraction patterns for the 5-gram scale accelerated aging reaction of **HMeIm** and CoO, with (**Hcaf**)(HSO<sub>4</sub>) (4 mol% with respect to CoO) as the ionic additive. The reaction mixture was prepared by 5 minute milling of reactants and the catalytic salt in a 25 mL stainless steel milling jar. The accelerated aging was conducted at 45 °C and 98% RH (from top to bottom): CoO reactant, **HMeIm** reactant; calculated pattern for ZIF-67 (CSD code GITTOT); reaction mixture after 10 days aging; 11 days aging; 13 days aging; 20 days aging; 25 days aging and the reaction product after calcination in air. The PXRD pattern of the calcined product corresponds to Co<sub>3</sub>O<sub>4</sub>.



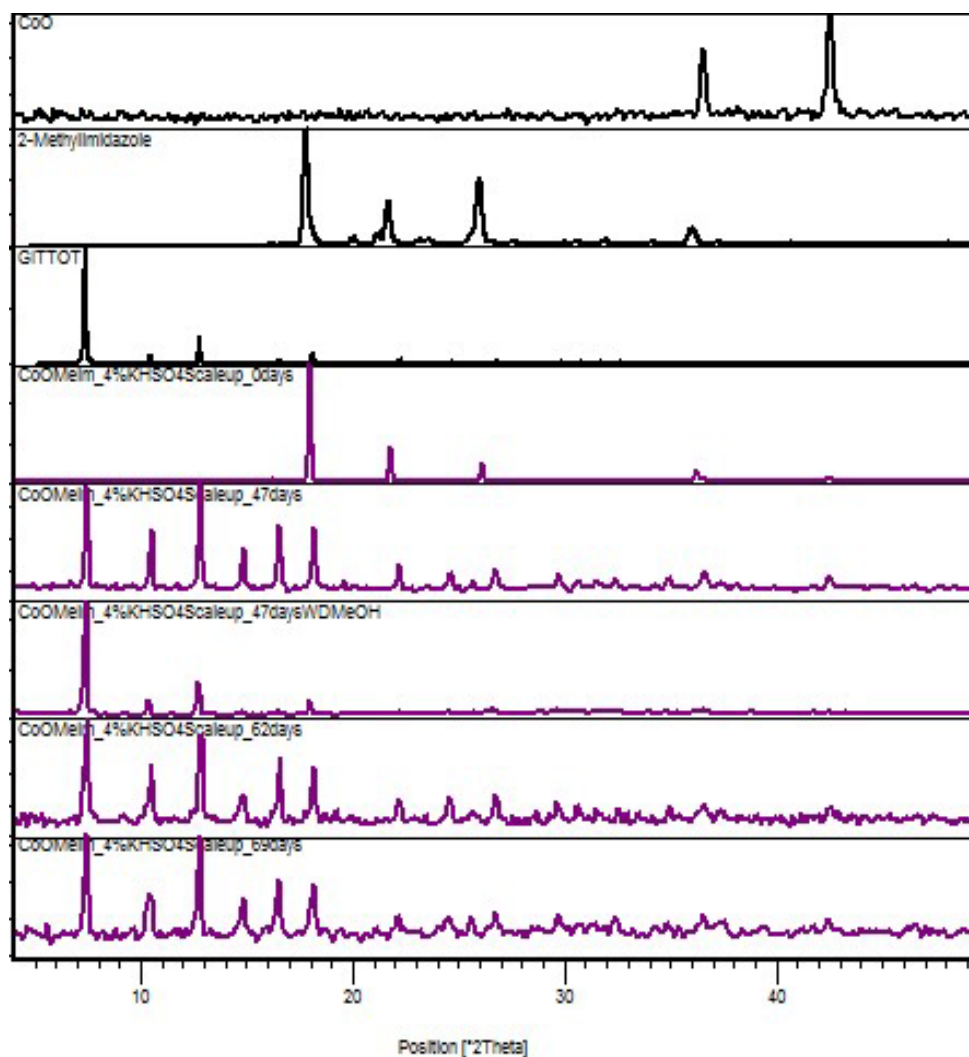
**Figure S12.** Powder X-ray diffraction patterns for the accelerated aging reaction of **HMeIm** and CoO, with KHSO<sub>4</sub> (4 mol% with respect to CoO) as the ionic additive. The reaction mixture was prepared by 5 minute milling of reactants and the catalytic salt in a 10 mL stainless steel milling jar. The accelerated aging was conducted at 45 °C and 98% RH (from top to bottom): CoO reactant, **HMeIm** reactant; calculated pattern for ZIF-67 (CSD code GITTOT); reaction mixture after 8 days; after 22 days; after 27 days; reaction mixture after 27 days accelerated aging, and evacuation; reaction mixture after 27 days accelerated aging, washed with water and reaction mixture after 27 days accelerated aging, washed with water and evacuated.



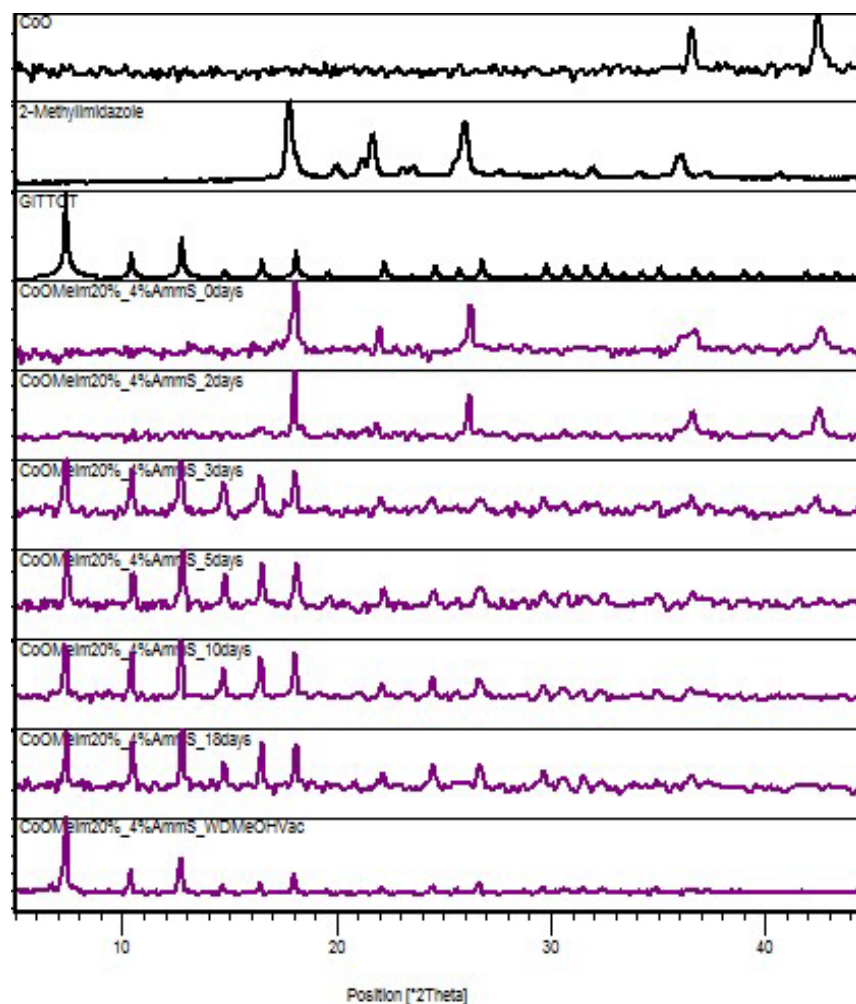
**Figure S13.** Powder X-ray diffraction patterns for the repeated accelerated aging reaction of **HMeIm** and CoO with KHSO<sub>4</sub> (4 mol% with respect to CoO) as the ionic additive. The reaction mixture was prepared by 5 minute milling of reactants and the catalytic salt in a 10 mL stainless steel milling jar. The accelerated aging was conducted at 45 °C and 98% RH (from top to bottom): CoO reactant, **HMeIm** reactant; calculated pattern for ZIF-67 (CSD code GITTOT); reaction mixture after 1 day; after 5 days; after 7 days; after 12 days; after 18 days; reaction mixture after 18 days accelerated aging and heating to 200 °C; ; reaction mixture after 18 days accelerated aging, washed with water; ; reaction mixture after 18 days accelerated aging, washed with water and evacuated; reaction mixture after 20 days accelerated aging; reaction mixture after 20 days accelerated aging, evacuated.



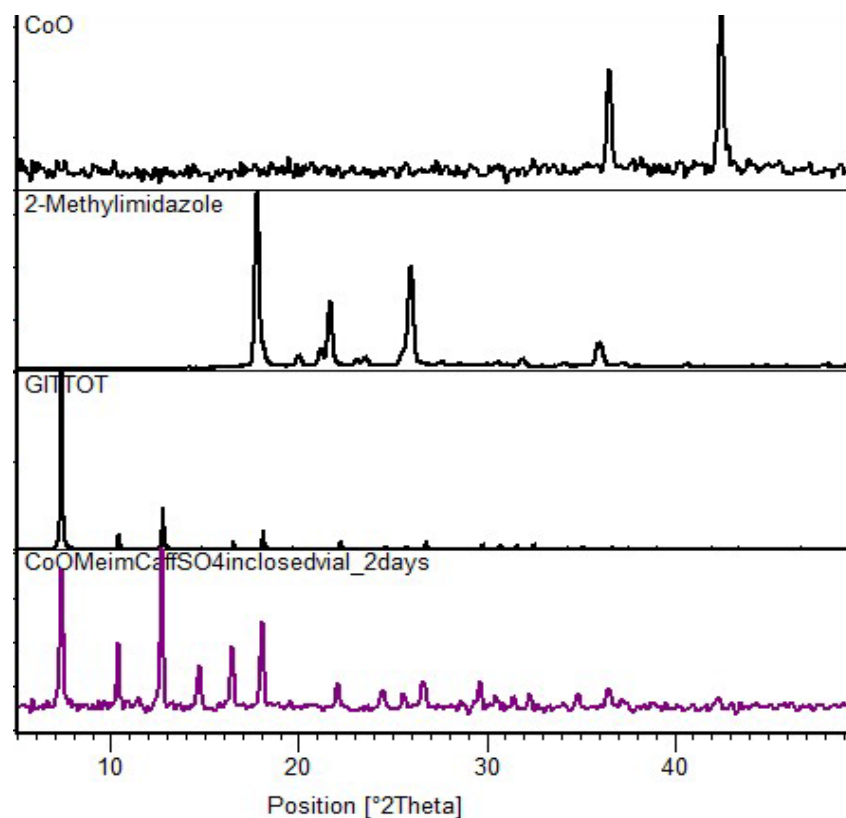
**Figure S14.** Powder X-ray diffraction patterns for the aging reaction of **HMeIm** and CoO without an ionic additive. The reaction mixture was prepared by 5 minute milling of reactants and the catalytic salt in a 10 mL stainless steel milling jar. Aging was conducted at 45 °C and 98% RH (from top to bottom): CoO reactant, **HMeIm** reactant; calculated pattern for ZIF-67 (CSD code GITTOT); reaction mixture immediately after mixing and after 5 days aging.



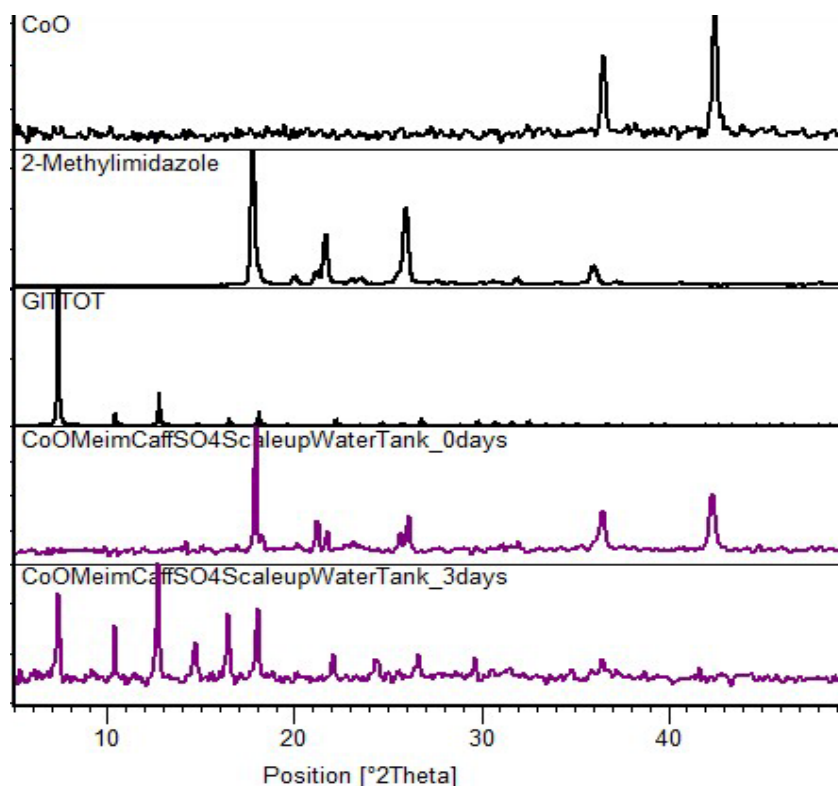




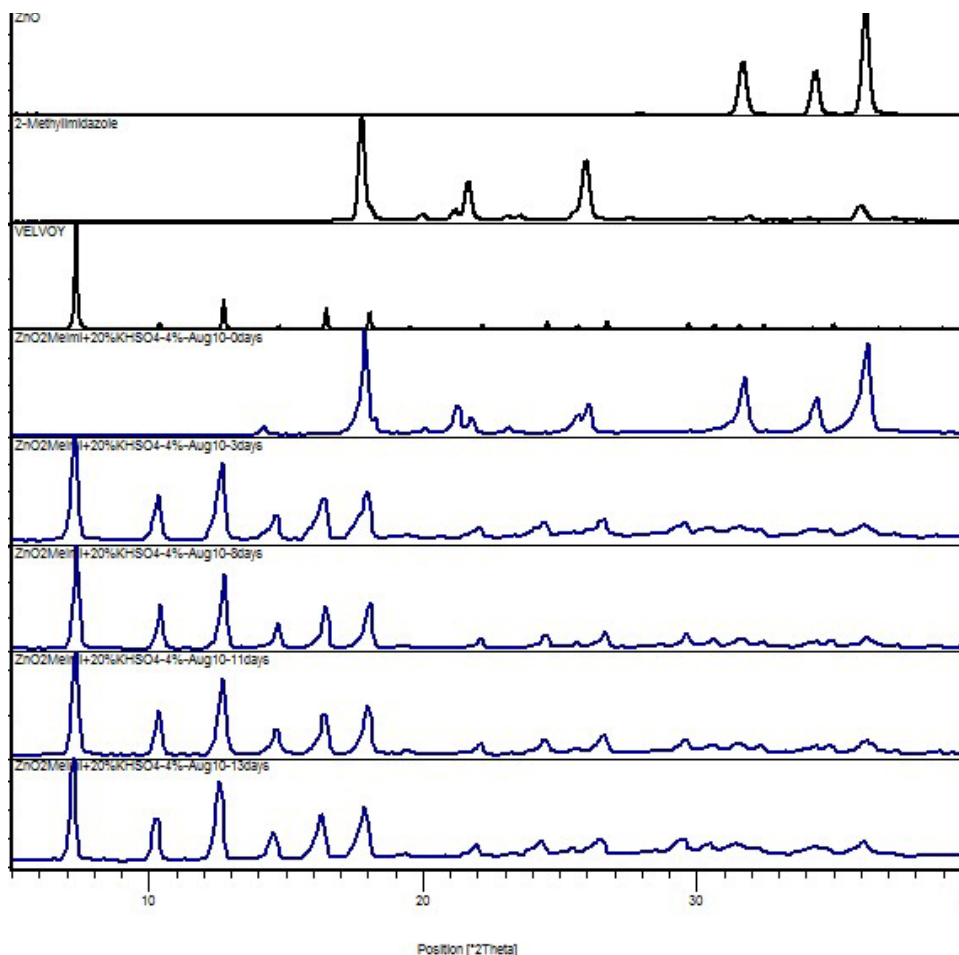
**Figure S16.** Powder X-ray diffraction patterns for the accelerated aging reaction of **HMeIm** and CoO with  $(\text{NH}_4)_2\text{SO}_4$  (4 mol% with respect to CoO) as the ionic additive. The reaction mixture was prepared by 5 minute milling of reactants and the catalytic salt in a 10 mL stainless steel milling jar. The accelerated aging was conducted at 45 °C and 98% RH (from top to bottom): CoO reactant, **HMeIm** reactant; calculated pattern for ZIF-67 (CSD code GITTOT); reaction mixture immediately after mixing; after 2 days; after 3 days; after 5 days; after 10 days; after 18 days; reaction mixture after 18 days accelerated aging, washed with methanol and evacuated.



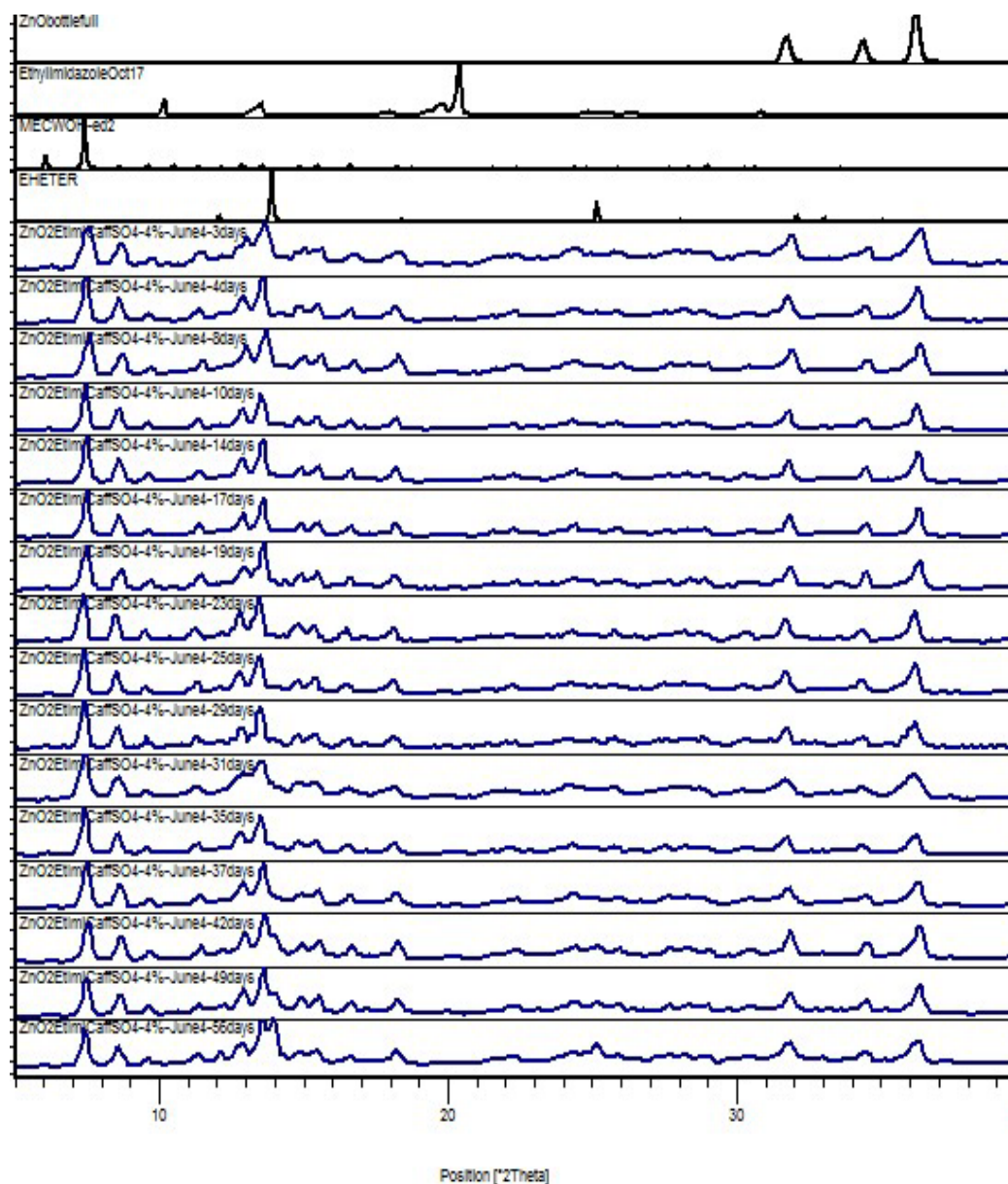
**Figure S17.** Powder X-ray diffraction patterns for the accelerated aging reaction of **HMeIm** and CoO with (**cafH**)(HSO<sub>4</sub>) (4 mol% with respect to CoO) as the ionic additive. The reaction mixture was prepared by 5 minute milling of reactants and the catalytic salt in a 10 mL stainless steel milling jar. The accelerated aging was conducted at 45 °C and 100% RH (from top to bottom): CoO reactant, **HMeIm** reactant; calculated pattern for ZIF-67 (CSD code GITTOT); reaction mixture after 2 days.



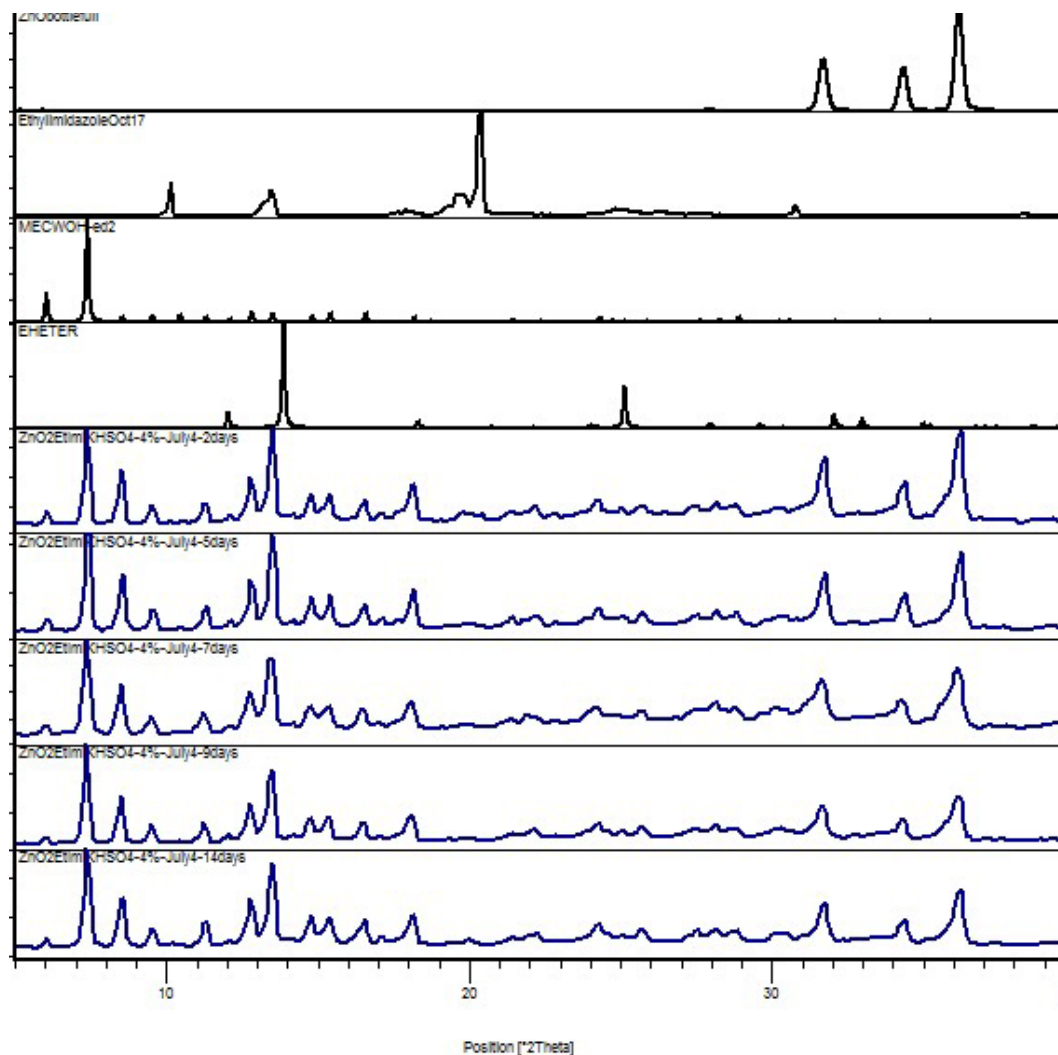
**Figure S18.** Powder X-ray diffraction patterns for the 5 gram accelerated aging reaction of **HMeIm** and CoO with (**cafH**)(H<sub>2</sub>SO<sub>4</sub>) (4 mol% with respect to CoO) as the ionic additive. The reaction mixture was prepared by 5 minute milling of reactants and the catalytic salt in a 10 mL stainless steel milling jar. The accelerated aging was conducted at 45 °C and 100% RH (from top to bottom): CoO reactant, **HMeIm** reactant; calculated pattern for ZIF-67 (CSD code GITTOT); reaction mixture immediately after mixing and after 3 days accelerated aging.



**Figure S19.** Powder X-ray diffraction patterns for the accelerated aging reaction of excess (20%) of **HMeIm** with ZnO in the presence of KHSO<sub>4</sub> (4 mol% with respect to ZnO) as the ionic additive. The reaction mixture was prepared by 5 minute milling of reactants and the catalytic salt in a 10 mL stainless steel milling jar. The accelerated aging was conducted at 45 °C and 98% RH (from top to bottom): ZnO reactant, **HMeIm** reactant; calculated pattern for ZIF-8 (CSD code VELVOY); reaction mixture immediately after mixing; after 3 days accelerated aging; after 8 days accelerated aging; after 11 days accelerated aging and after 13 days accelerated aging.

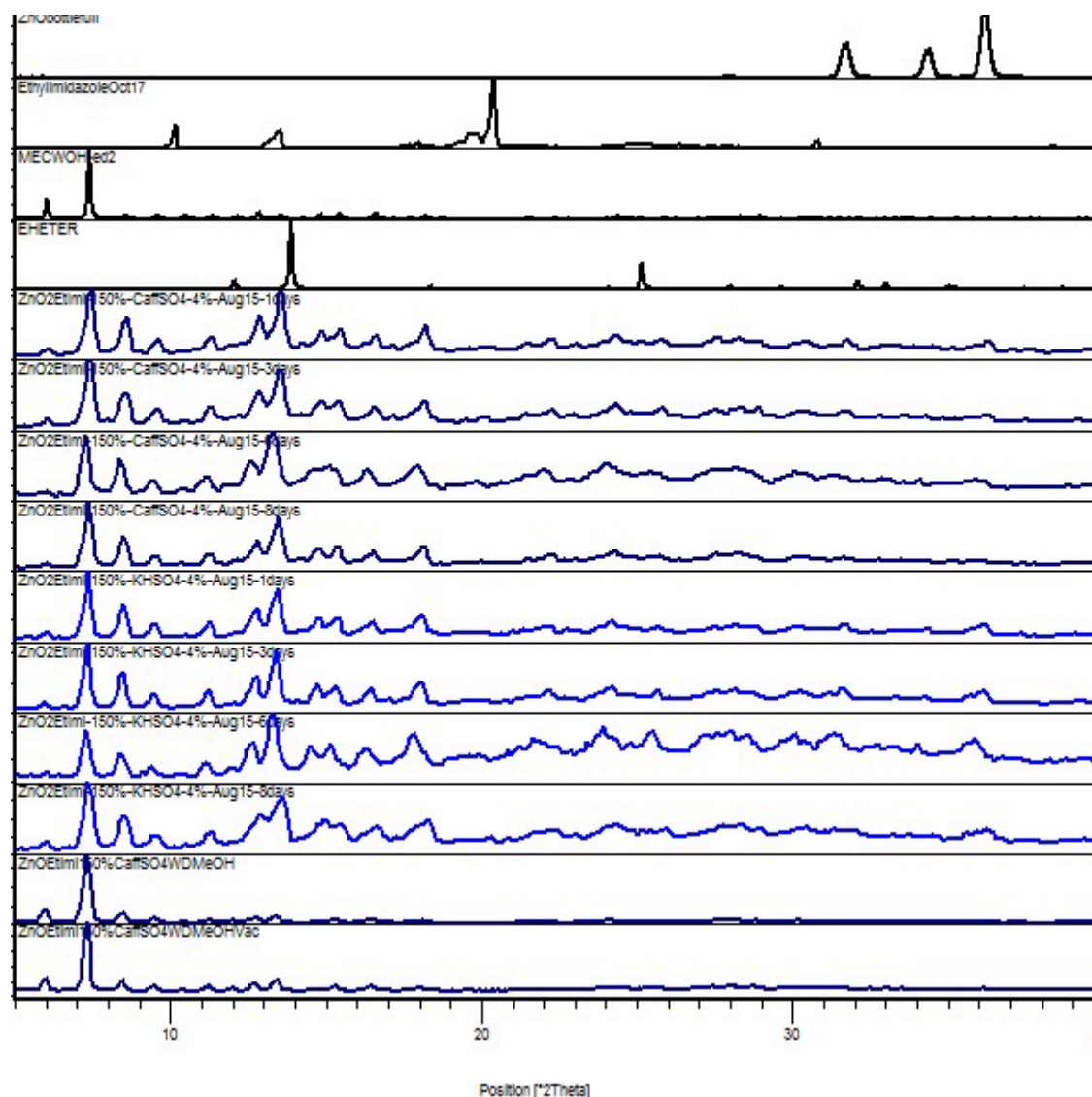


**Figure S20.** Powder X-ray diffraction patterns for the accelerated aging reaction of **HEtIm** with ZnO in the presence of (**cafH**)(HSO<sub>4</sub>) (4 mol% with respect to ZnO) as the ionic additive. The reaction mixture was prepared by 5 minute milling of reactants and the catalytic salt in a 10 mL stainless steel milling jar. The accelerated aging was conducted at 45 °C and 98% RH (from top to bottom): ZnO reactant, **HEtIm** reactant; calculated pattern for zeolite rho topology Zn(**EtIm**)<sub>2</sub> porous framework (CSD code MECWOH); calculated pattern for quartz topology non-porous Zn(**EtIm**)<sub>2</sub> framework (CSD code EHETER); reaction mixture after 3 days accelerated aging; after 4 days accelerated aging; after 8 days accelerated aging; after 10 days accelerated aging; after 14 days accelerated aging; after 17 days accelerated aging; after 19 days accelerated aging; after 23 days accelerated aging; after 25 days accelerated aging; after 29 days accelerated aging; after 31 days accelerated aging; after 35 days accelerated aging; after 37 days accelerated aging; after 42 days accelerated aging; after 49 days accelerated aging and after 56 days accelerated aging.

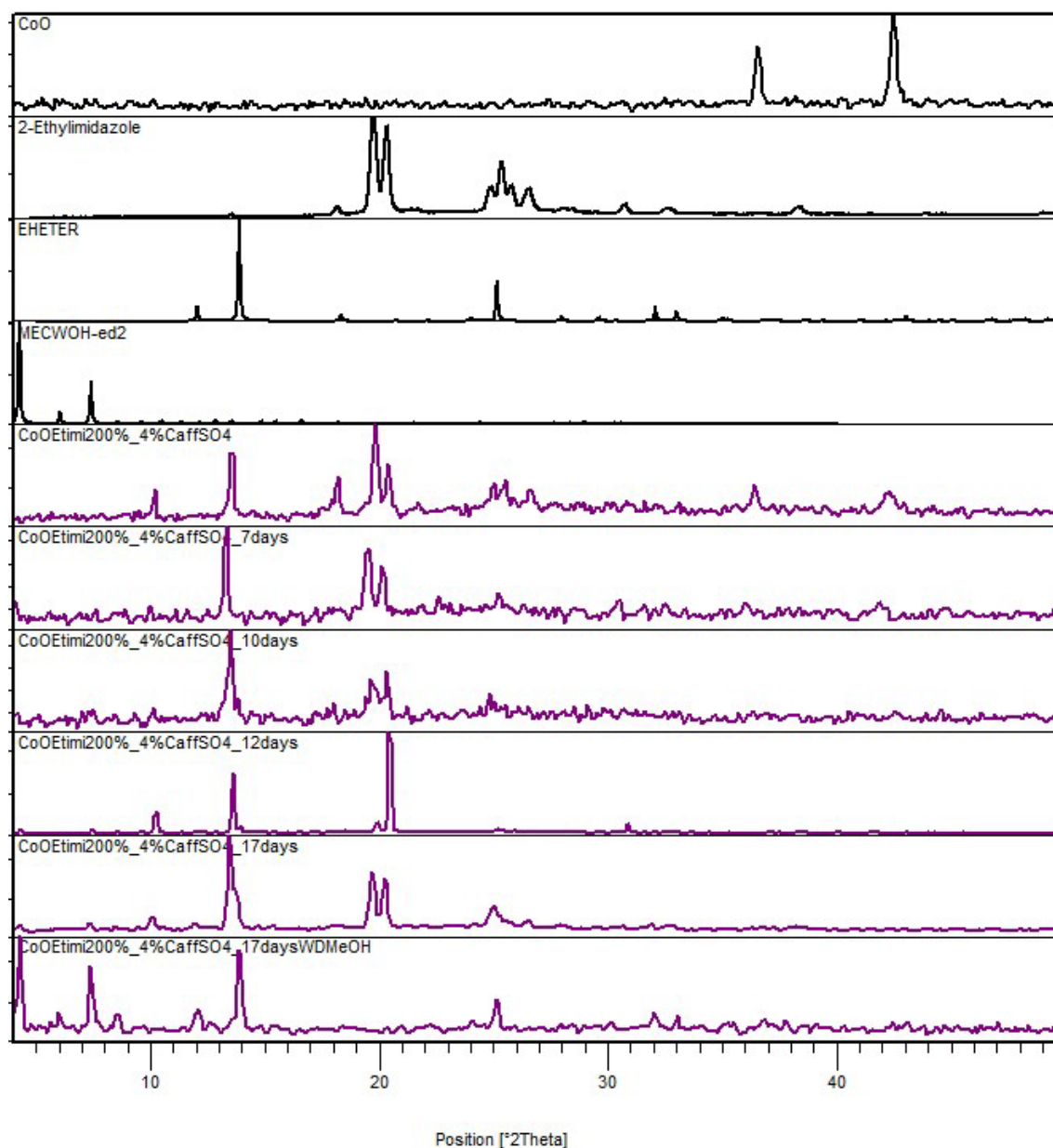


**Figure S21.** Powder X-ray diffraction patterns for the accelerated aging reaction of **HEtIm** with ZnO in the presence of KHSO<sub>4</sub> (4 mol% with respect to ZnO) as the ionic additive. The reaction mixture was prepared by 5 minute milling of reactants and the catalytic salt in a 10 mL stainless steel milling jar. The accelerated aging was conducted at 45 °C and 98% RH (from top to bottom): ZnO reactant, **HEtIm** reactant; calculated pattern for zeolite rho topology Zn(**EtIm**)<sub>2</sub> porous framework (CSD code MECWOH); calculated pattern for quartz topology non-porous Zn(**EtIm**)<sub>2</sub> framework (CSD code EHETER); reaction mixture after 2 days accelerated aging; after 5 days accelerated aging; after 7 days accelerated aging; after 9 days accelerated aging and after 14 days accelerated aging.

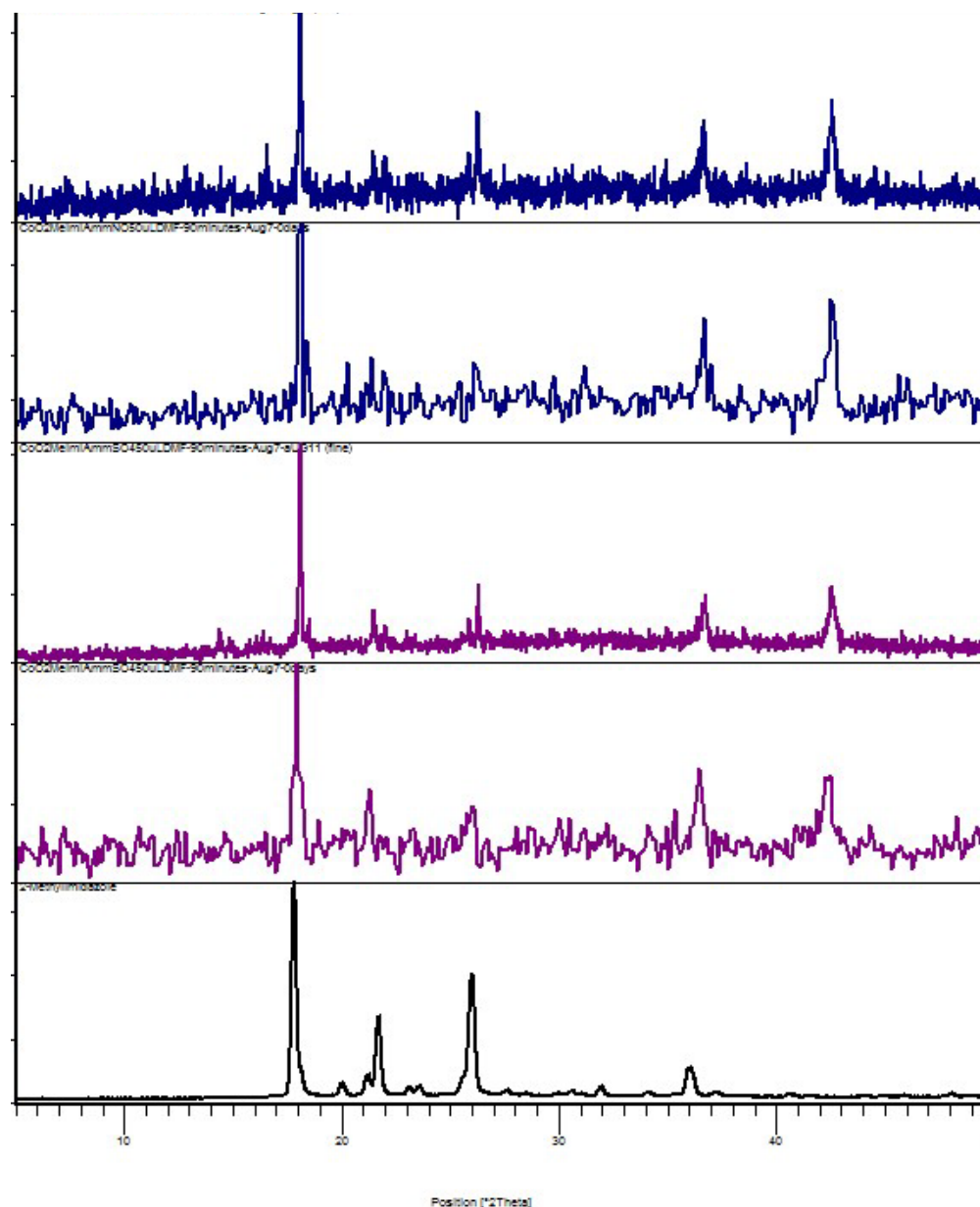




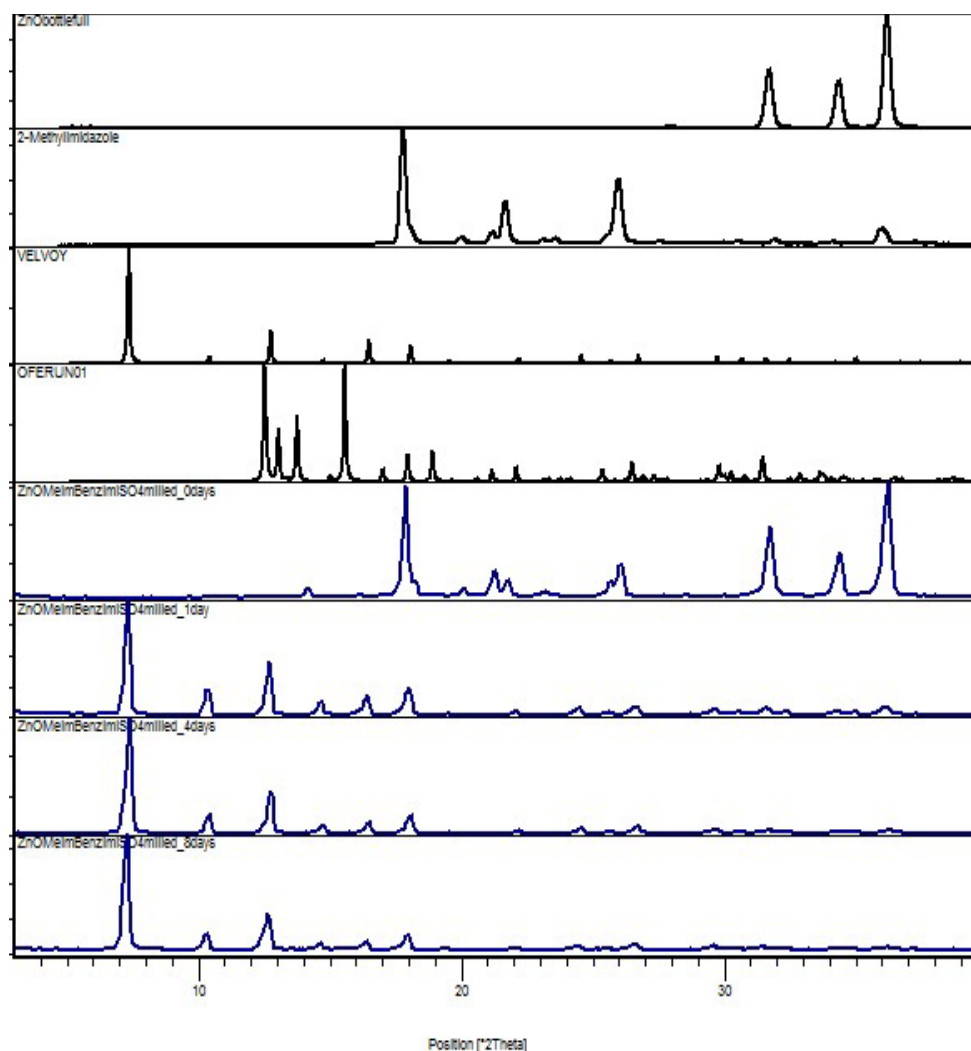
**Figure S22.** Powder X-ray diffraction patterns for the accelerated aging reaction of excess (150%) **HEtIm** with ZnO in the presence of either KHSO<sub>4</sub> or (**cafH**)(HSO<sub>4</sub>) (each 4 mol% with respect to ZnO) as the ionic additive. The reaction mixtures were prepared by 5 minute milling of reactants and the salt additive in a 10 mL stainless steel milling jar. The accelerated aging was conducted at 45 °C and 98% RH (from top to bottom): ZnO reactant, **HEtIm** reactant; calculated pattern for zeolite rho topology Zn(**EtIm**)<sub>2</sub> porous framework (CSD code MECWOH); calculated pattern for quartz topology non-porous Zn(**EtIm**)<sub>2</sub> framework (CSD code EHETER); reaction mixture with (**cafH**)(HSO<sub>4</sub>) after 1 day accelerated aging; reaction mixture with (**cafH**)(HSO<sub>4</sub>) after 3 days accelerated aging; reaction mixture with (**cafH**)(HSO<sub>4</sub>) after 6 days accelerated aging; reaction mixture with (**cafH**)(HSO<sub>4</sub>) after 8 days accelerated aging; reaction mixture with KHSO<sub>4</sub> after 1 day accelerated aging; reaction mixture with KHSO<sub>4</sub> after 3 days accelerated aging; reaction mixture with KHSO<sub>4</sub> after 6 days accelerated aging; reaction mixture with KHSO<sub>4</sub> after 8 days accelerated aging; product of accelerating aging with (**cafH**)(HSO<sub>4</sub>) additive after washing with methanol and after washing with methanol followed by evacuation.



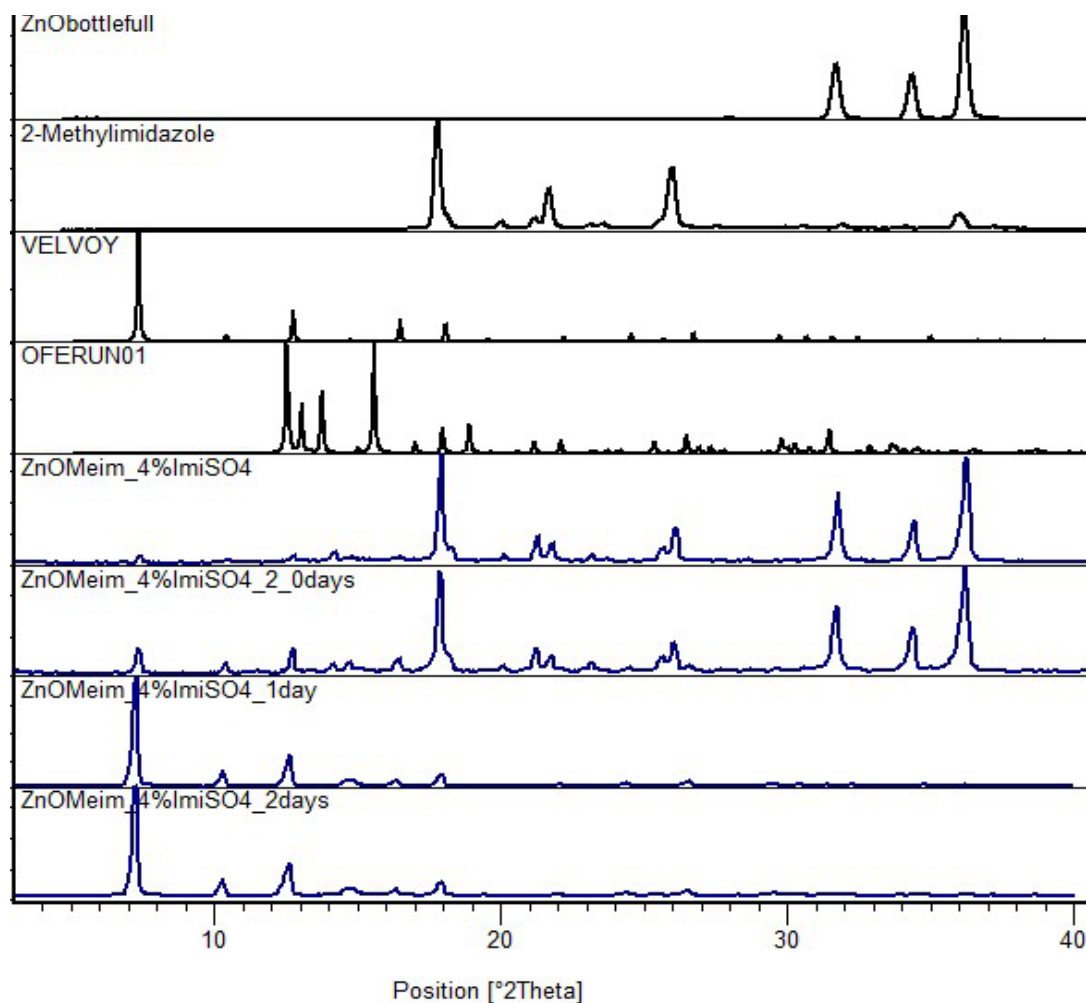
**Figure S23.** Powder X-ray diffraction patterns for the accelerated aging reaction of excess (200%) **HEtIm** with CoO in the presence of (cafH)(H<sub>2</sub>SO<sub>4</sub>) (4 mol% with respect to CoO) as the ionic additive. The reaction mixtures were prepared by 5 minute milling of reactants and the salt additive in a 10 mL stainless steel milling jar. The accelerated aging was conducted at 45 °C and 98% RH (from top to bottom): CoO reactant, **HEtIm** reactant; calculated pattern for quartz topology non-porous Zn(**EtIm**)<sub>2</sub> framework (CSD code EHETER); calculated pattern for zeolite rho topology Zn(**EtIm**)<sub>2</sub> porous framework (CSD code MECWOH); reaction mixture after 1 day accelerated aging; reaction mixture after 7 days accelerated aging; reaction mixture after 10 days accelerated aging; reaction mixture after 12 days accelerated aging; reaction mixture after 17 days accelerated aging and reaction mixture after 17 days accelerated aging, washed with methanol. Before washing with methanol, the PXRD patterns are dominated by the excess **HEtIm** ligand.



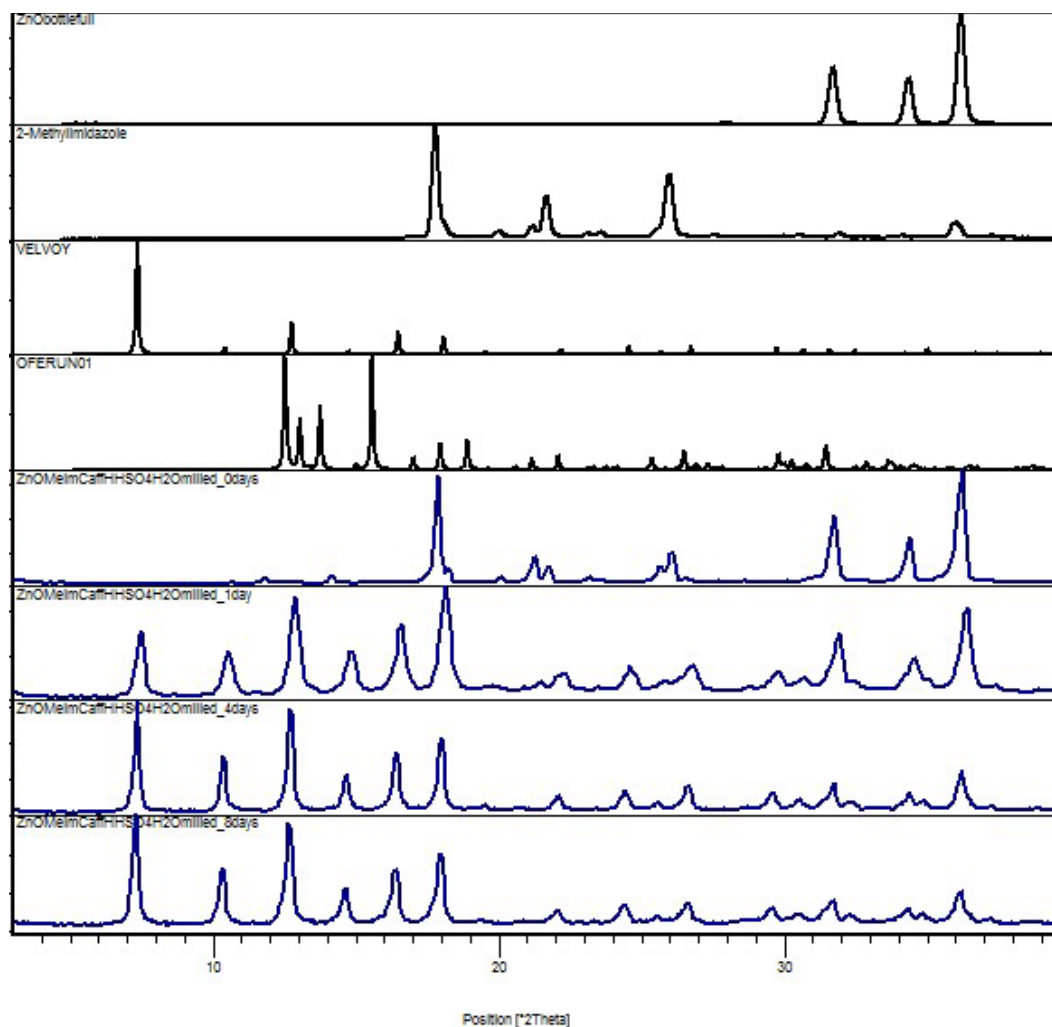
**Figure S24.** Powder X-ray diffraction patterns for attempted ion- and liquid-assisted (ILAG) mechanochemical syntheses of ZIF-67 (from top to bottom): mixture of CoO and **HMeIm** milled for 90 minutes in the presence of DMF and ammonium nitrate additive after 4 days sitting in a vial; mixture of CoO and **HMeIm** milled for 90 minutes in the presence of DMF and ammonium nitrate; mixture of CoO and **HMeIm** milled for 90 minutes in the presence of DMF and ammonium sulfate additive after 4 days sitting in a vial; mixture of CoO and **HMeIm** milled for 90 minutes in the presence of DMF and ammonium nitrate and commercial **HMeIm**. The reactions were designed to mimic the ones previously reported for the synthesis of ZIF-8 from ZnO, but the milling time was tripled (see: P. J. Beldon, L. Fábíán, R. S. Stein, A. Thirumurugan, A. K. Cheetham, T. Frišćić, *Angew. Chem. Int. Ed.*, **2010**, 49, 9640)



**Figure S25.** Powder X-ray diffraction patterns for the accelerated aging reaction of **HMeIm** with ZnO in the presence of **(HBIIm)<sub>2</sub>(SO<sub>4</sub>)** (4 mol% with respect to ZnO) as the ionic additive. The reaction mixture was prepared by 5 minute milling of reactants and the salt additive in a 10 mL stainless steel milling jar. The accelerated aging was conducted at 45 °C and 100% RH (from top to bottom): ZnO reactant, **HMeIm** reactant; calculated pattern for the ZIF-8 sodalite-type framework (CSD code VELVOY); calculated pattern for the non-porous diamondoid Zn(**MeIm**)<sub>2</sub> framework (CSD code OFERUN01); reaction mixture immediately after mixing; after 1 day accelerated aging; after 4 days accelerated aging and after 8 days accelerated aging.

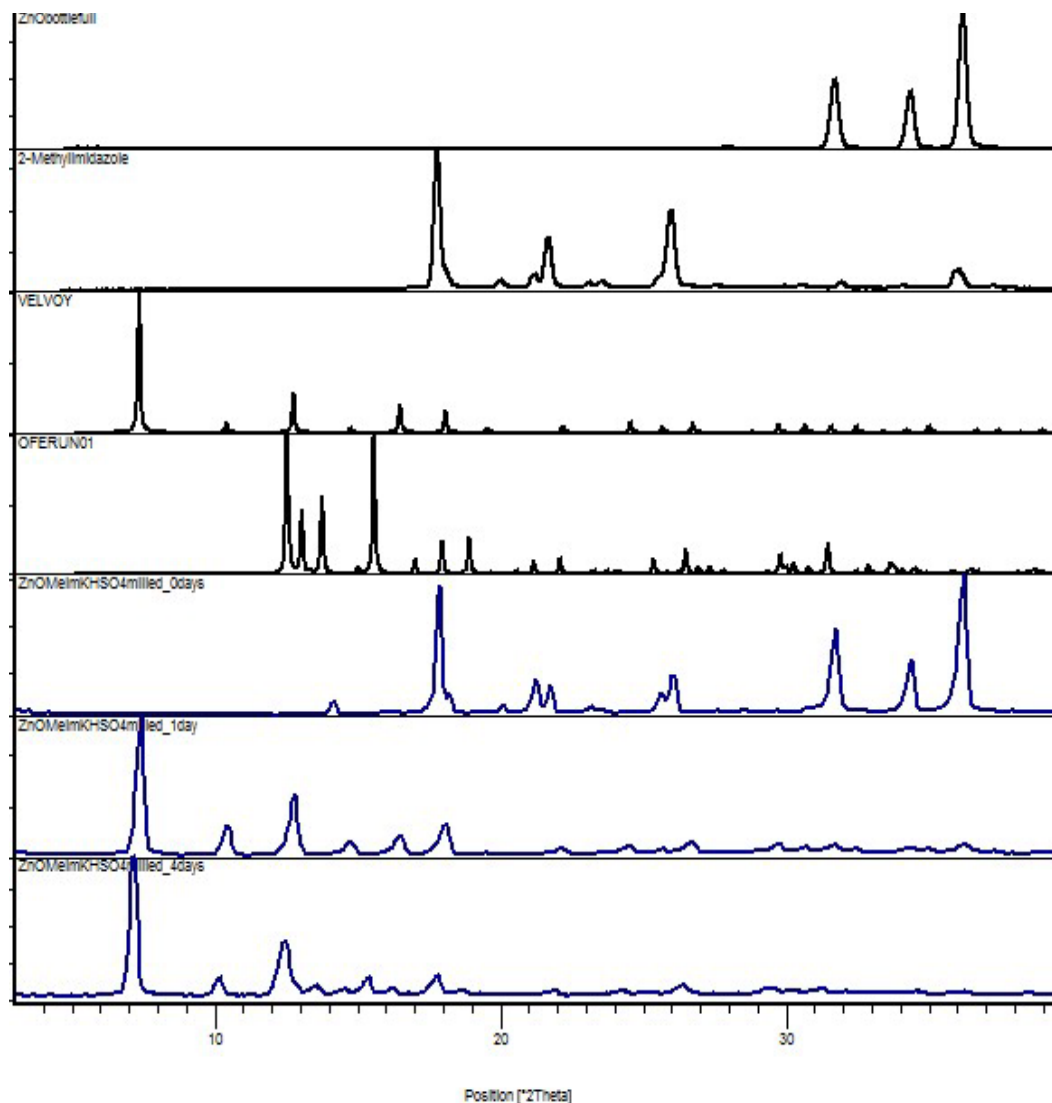


**Figure S26.** Powder X-ray diffraction patterns for the accelerated aging reaction of **HMeIm** with ZnO in the presence of  $(\text{H}_2\text{Im})_2(\text{SO}_4) \cdot 2\text{H}_2\text{O}$  (4 mol% with respect to ZnO) as the ionic additive. The reaction mixture was prepared by 5 minute milling of reactants and the salt additive in a 10 mL stainless steel milling jar. The accelerated aging was conducted at 45 °C and 100% RH (from top to bottom): ZnO reactant, **HMeIm** reactant; calculated pattern for the ZIF-8 sodalite-type framework (CSD code VELVOY); calculated pattern for the non-porous diamondoid  $\text{Zn}(\text{MeIm})_2$  framework (CSD code OFERUN01); reaction mixture immediately after mixing; another identically prepared reaction mixture immediately after mixing; reaction mixture after 1 day accelerated aging and after 2 days accelerated aging.

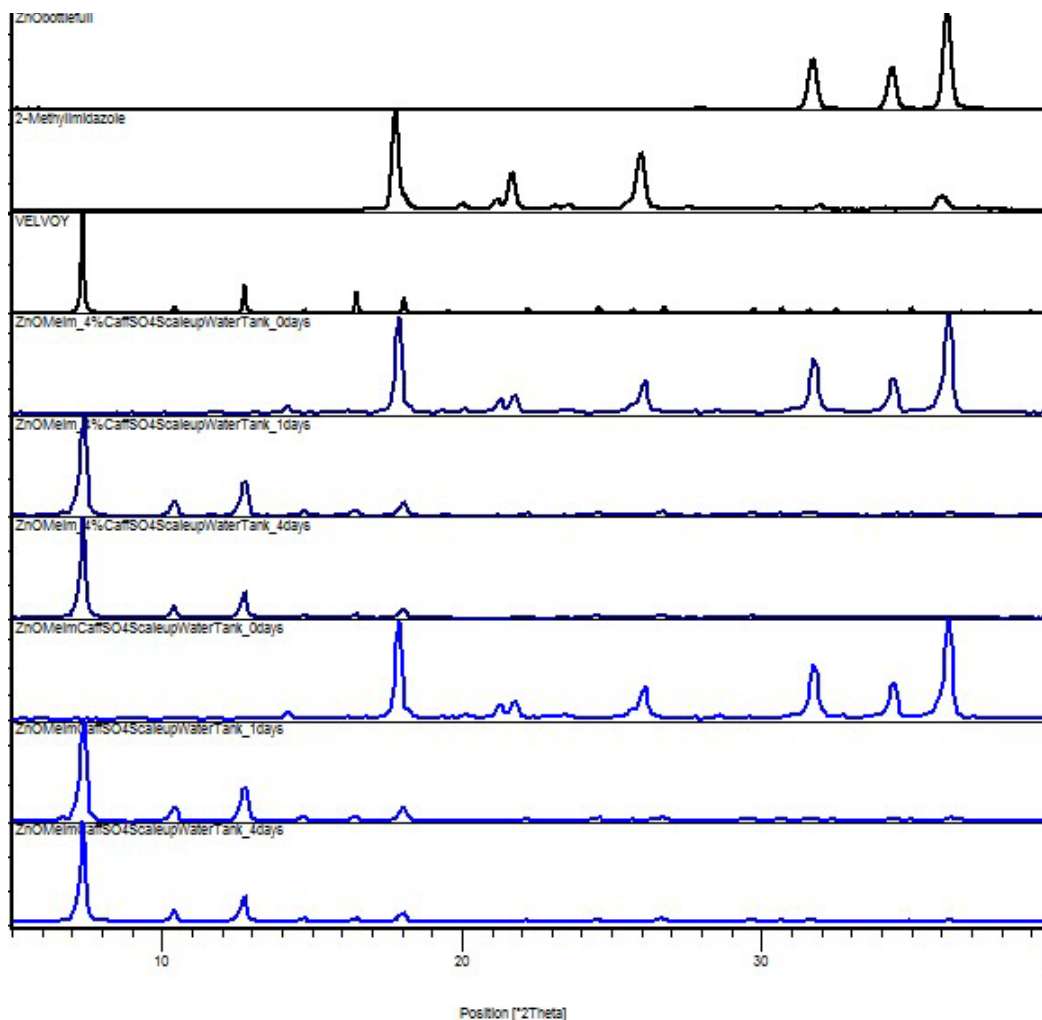


**Figure S27.** Powder X-ray diffraction patterns for the accelerated aging reaction of **HMeIm** with ZnO in the presence of (**Hcaf**)(HSO<sub>4</sub>)·H<sub>2</sub>O (4 mol% with respect to ZnO) as the ionic additive. The reaction mixture was prepared by 5 minute milling of reactants and the salt additive in a 10 mL stainless steel milling jar. The accelerated aging was conducted at 45 °C and 100% RH (from top to bottom): ZnO reactant, **HMeIm** reactant; calculated pattern for the ZIF-8 sodalite-type framework (CSD code VELVOY); calculated pattern for the non-porous diamondoid Zn(**MeIm**)<sub>2</sub> framework (CSD code OFERUN01); reaction mixture immediately after mixing; reaction mixture after 1 day accelerated aging; after 4 days accelerated aging and after 8 days accelerated aging.

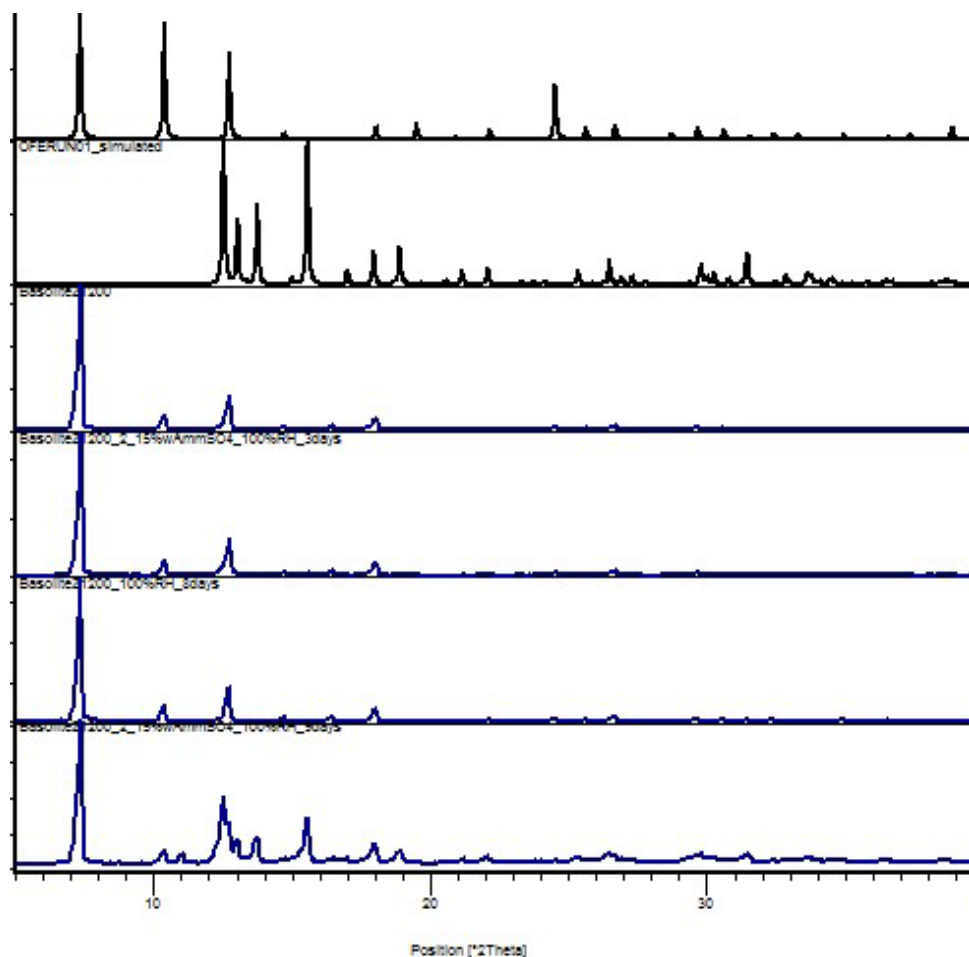




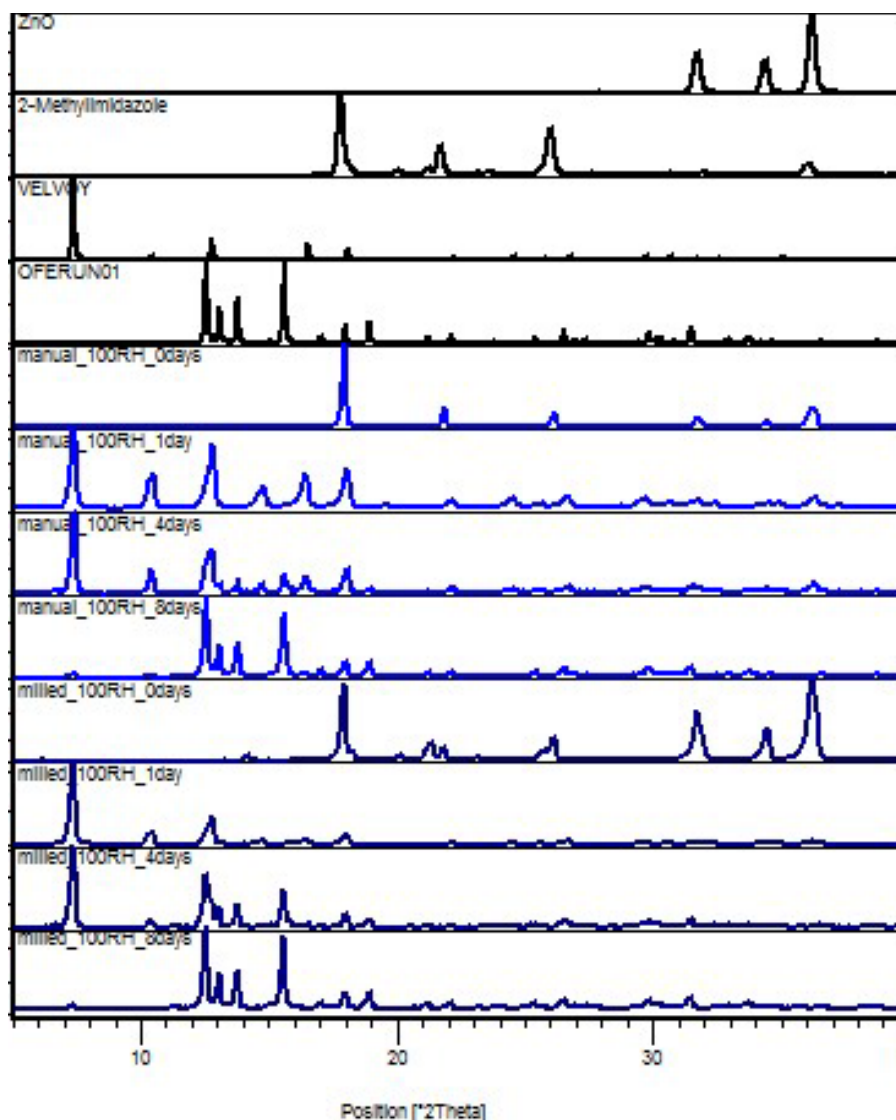
**Figure S28.** Powder X-ray diffraction patterns for the accelerated aging reaction of **HMeIm** with ZnO in the presence of KHSO<sub>4</sub> (4 mol% with respect to ZnO) as the ionic additive. The reaction mixture was prepared by 5 minute milling of reactants and the salt additive in a 10 mL stainless steel milling jar. The accelerated aging was conducted at 45 °C and 100% RH (from top to bottom): ZnO reactant, **HMeIm** reactant; calculated pattern for the ZIF-8 sodalite-type framework (CSD code VELVOY); calculated pattern for the non-porous diamondoid Zn(**MeIm**)<sub>2</sub> framework (CSD code OFERUN01); reaction mixture immediately after mixing; reaction mixture after 1 day accelerated aging and after 4 days accelerated aging.



**Figure S29.** Powder X-ray diffraction patterns for two identically prepared 5 gram scale accelerated aging reaction of **HMeIm** with ZnO in the presence of (**Hcaf**)(H<sub>2</sub>SO<sub>4</sub>) (4 mol% with respect to ZnO) as the ionic additive. The reaction mixture was prepared by 5 minute milling of reactants and the salt additive in a 25 mL stainless steel milling jar. The accelerated aging was conducted at 45 °C and 100% RH (from top to bottom): ZnO reactant, **HMeIm** reactant; calculated pattern for the ZIF-8 sodalite-type framework (CSD code VELVOY); first reaction mixture immediately after mixing; first reaction mixture after 1 day accelerated aging; first reaction mixture after 4 days accelerated aging; second reaction mixture immediately after mixing; second reaction mixture after 1 day accelerated aging and second reaction mixture after 4 days accelerated aging.

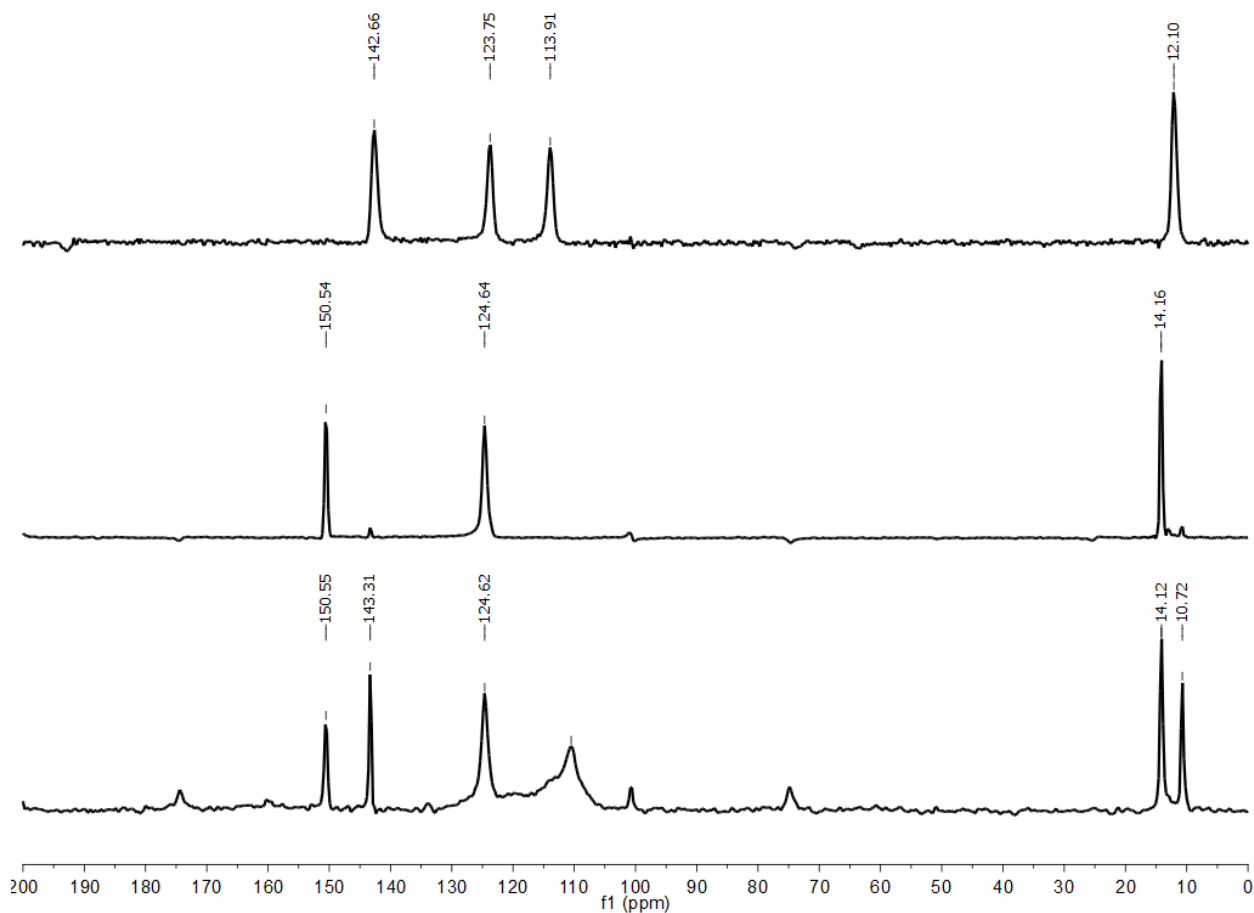


**Figure S30.** Powder X-ray diffraction patterns for the aging degradation of commercial ZIF-8 (Basolite Z1200) in the presence of 4 mol% ammonium sulfate (from top to bottom): simulated pattern for the ZIF-8 structure; simulated pattern for the close-packed *dia*-Zn(MeIm)<sub>2</sub>; initial sample of Basolite Z1200; Basolite Z1200 after three days at 45 °C and 100% RH with 4 mol% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>; Basolite Z1200 after eight days in 100% RH with 4 mol% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and Basolite Z1200 after nine days in 100% RH with 4 mol% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.

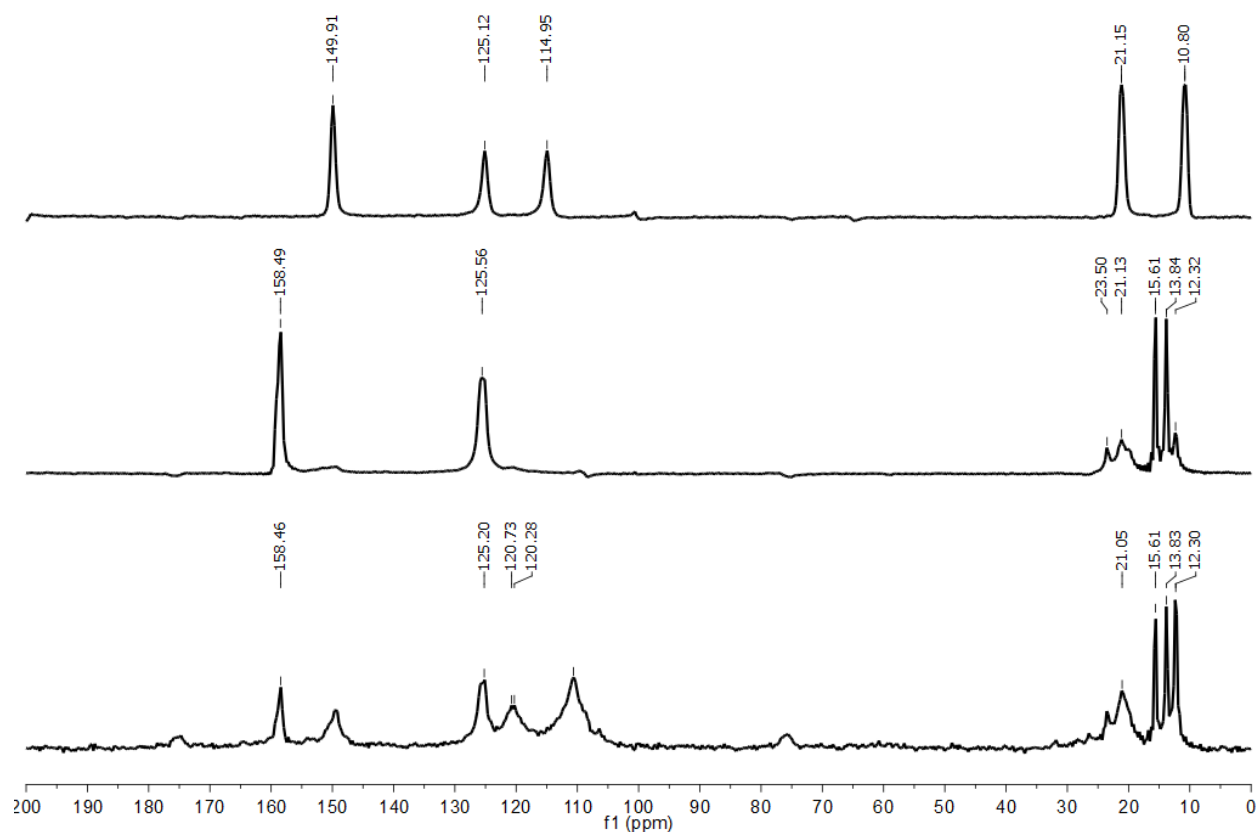


**Figure S31.** Powder X-ray diffraction patterns for the course of the accelerated aging reaction of ZnO and HMeIm using 4 mol% ammonium sulfate as the ionic additive, with reaction mixtures prepared either by manual mixing (blue) or mixed by ball milling for 5 minutes (dark blue) (from top to bottom): commercial ZnO, commercial **HMeIm**, simulated pattern for the ZIF-8 structure; simulated pattern for the close-packed *dia*-Zn(**MeIm**)<sub>2</sub>; manually prepared mixture immediately after mixing, after 1 day, four days and 8 days aging at 45 °C and 100% RH; milled mixture immediately after mixing, after one day, four days and eight days of aging at 45°C and 100% RH. The results strongly suggest very little difference between reaction mixtures mixed manually or by brief milling.

### 3. SOLID-STATE NMR SPECTROSCOPY DATA

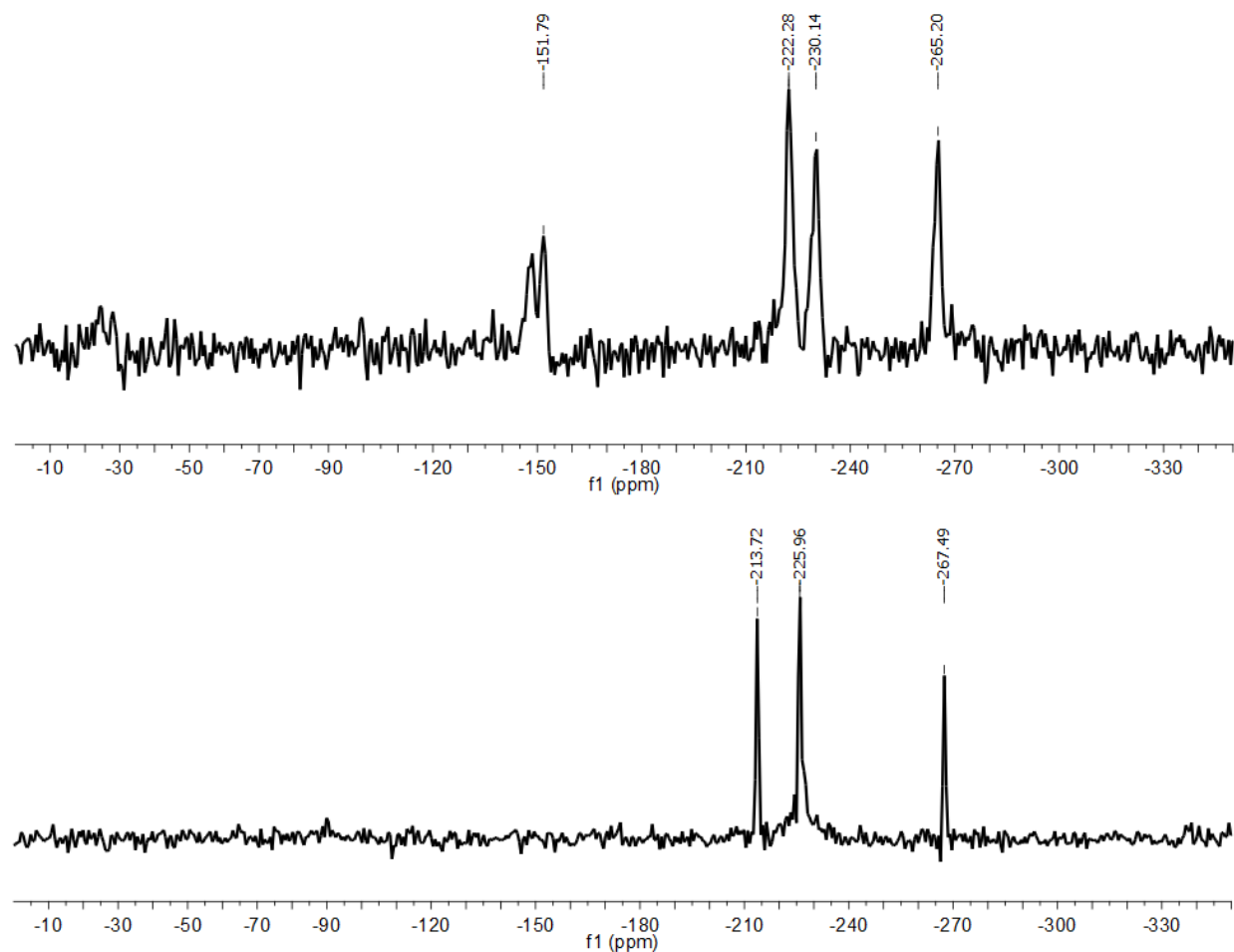


**Figure S32.**  $^{13}\text{C}$  SSNMR spectra for reactions of  $\text{ZnO}$  and **HMeIm**, in the presence of 20% excess **HMeIm** and 4 mol%  $\text{KHSO}_4$  ionic additive: (top) CP-MAS spectrum of crystalline **HMeIm**; (center) CP-MAS spectrum of the ZIF-8 structure  $\text{Zn}(\text{MeIm})_2$  obtained by accelerated aging and (bottom) DP-MAS spectrum of the ZIF-8 structure  $\text{Zn}(\text{MeIm})_2$  obtained by accelerated aging. Signal at 110 ppm corresponds to the teflon spacer of the sample holder.



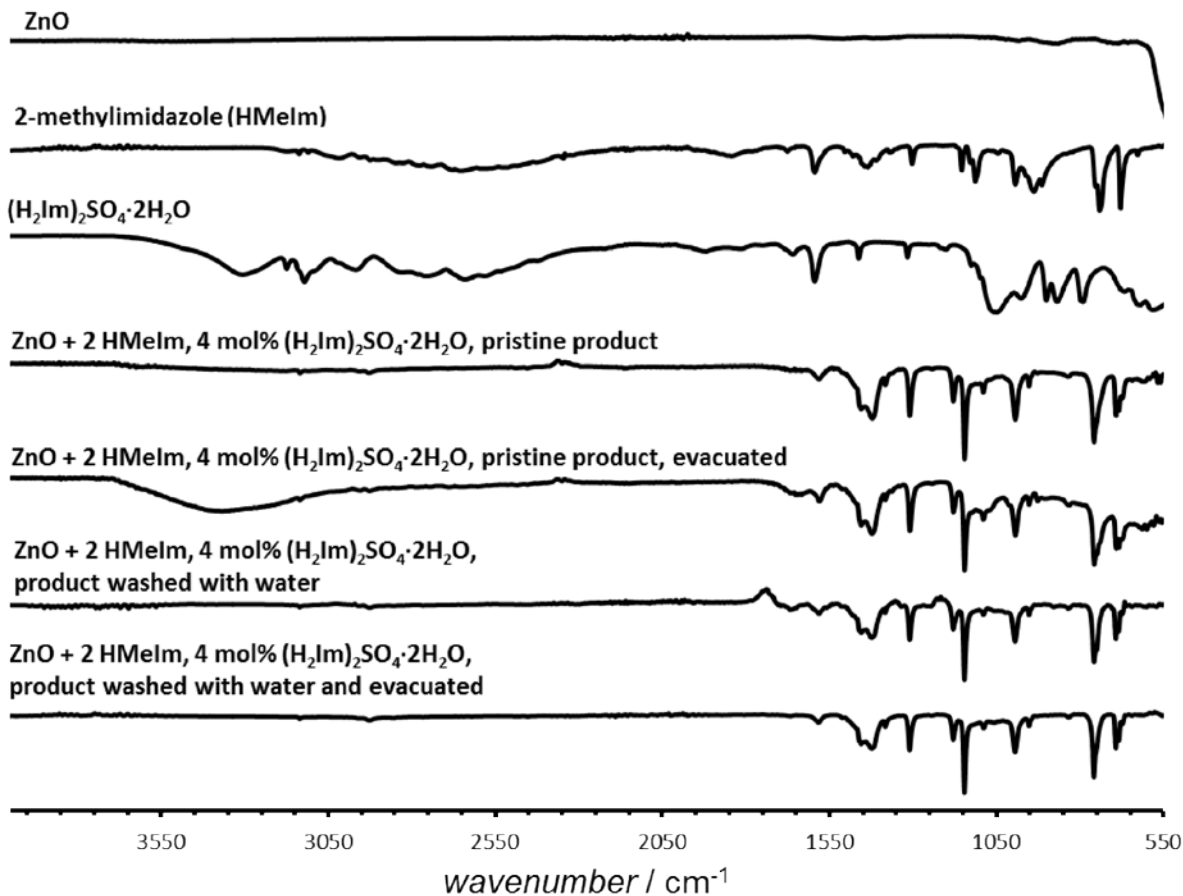
**Figure S33.**  $^{13}\text{C}$  SSNMR spectra for reactions of ZnO and **HEtIm**, in the presence of 150% excess **HEtIm** and 4 mol% (**Hcaf**)( $\text{HSO}_4$ ) ionic additive: (top) CP-MAS spectrum of crystalline **HEtIm**; (center) CP-MAS spectrum of the  $\text{RHO-Zn(EtIm)}_2$  obtained by accelerated aging and (bottom) DP-MAS spectrum of the  $\text{RHO-Zn(EtIm)}_2$  made by accelerated aging. Signal at 110 ppm corresponds to the teflon spacer of the sample holder.



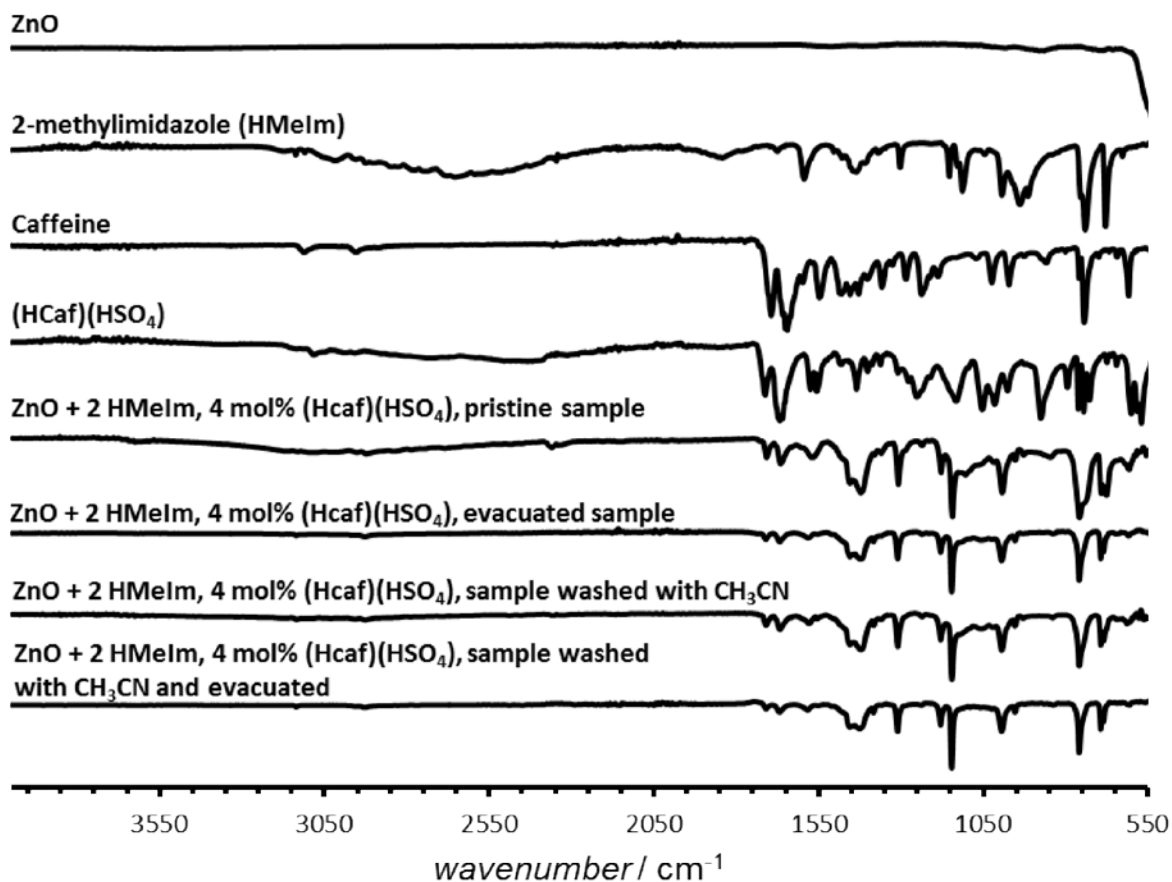


**Figure S34.** Natural abundance  $^{15}\text{N}$  SSNMR spectra for commercial caffeine (top) and  $(\text{Hcaf})(\text{HSO}_4)$  (bottom). The pattern of NMR signals for  $(\text{Hcaf})(\text{HSO}_4)$  is consistent with the one previously reported for protonated caffeine in solid salts, see T. Friščić, D. G. Reid, G. M. Day, M. J. Duer, W. Jones, *Cryst. Growth Des.* **2011**, *11*, 972-981.

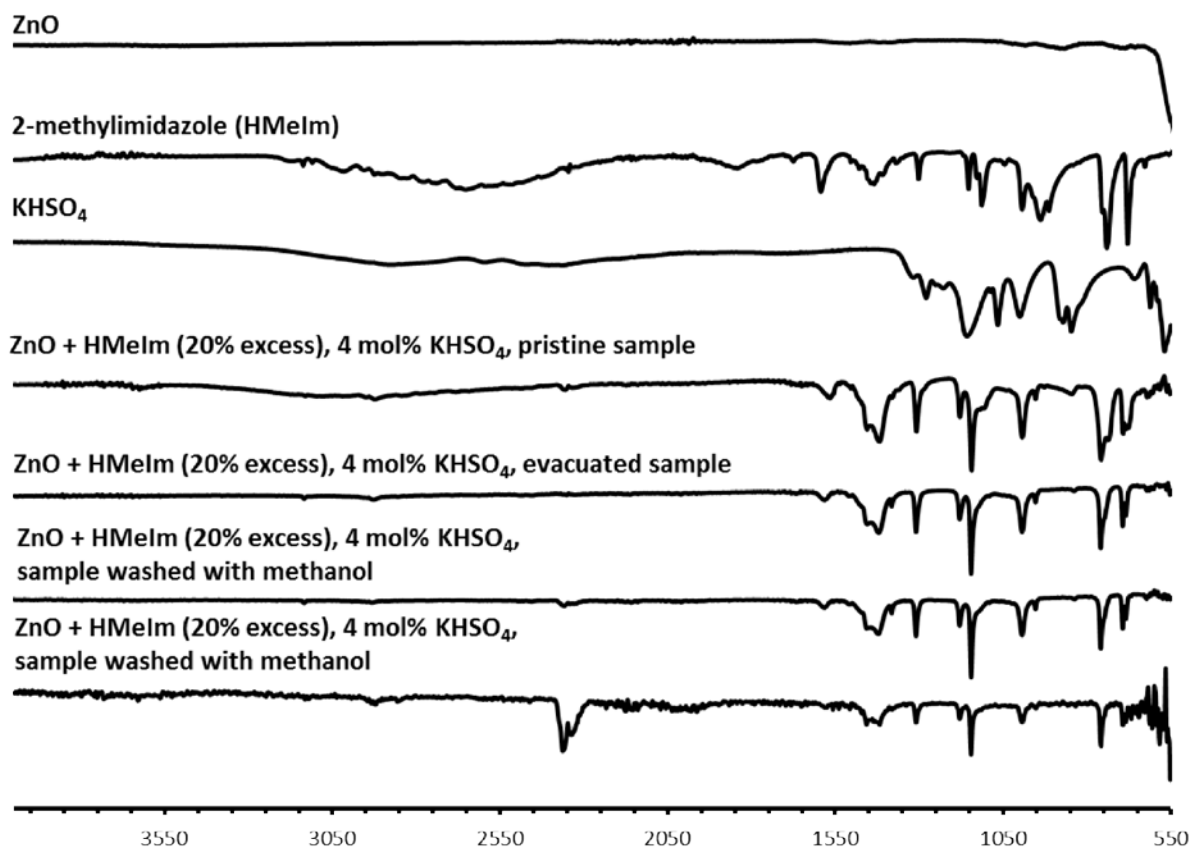
#### 4. SELECTED FOURIER-TRANSFORM ATTENUATED TOTAL REFLECTION (FTIR-ATR) DATA



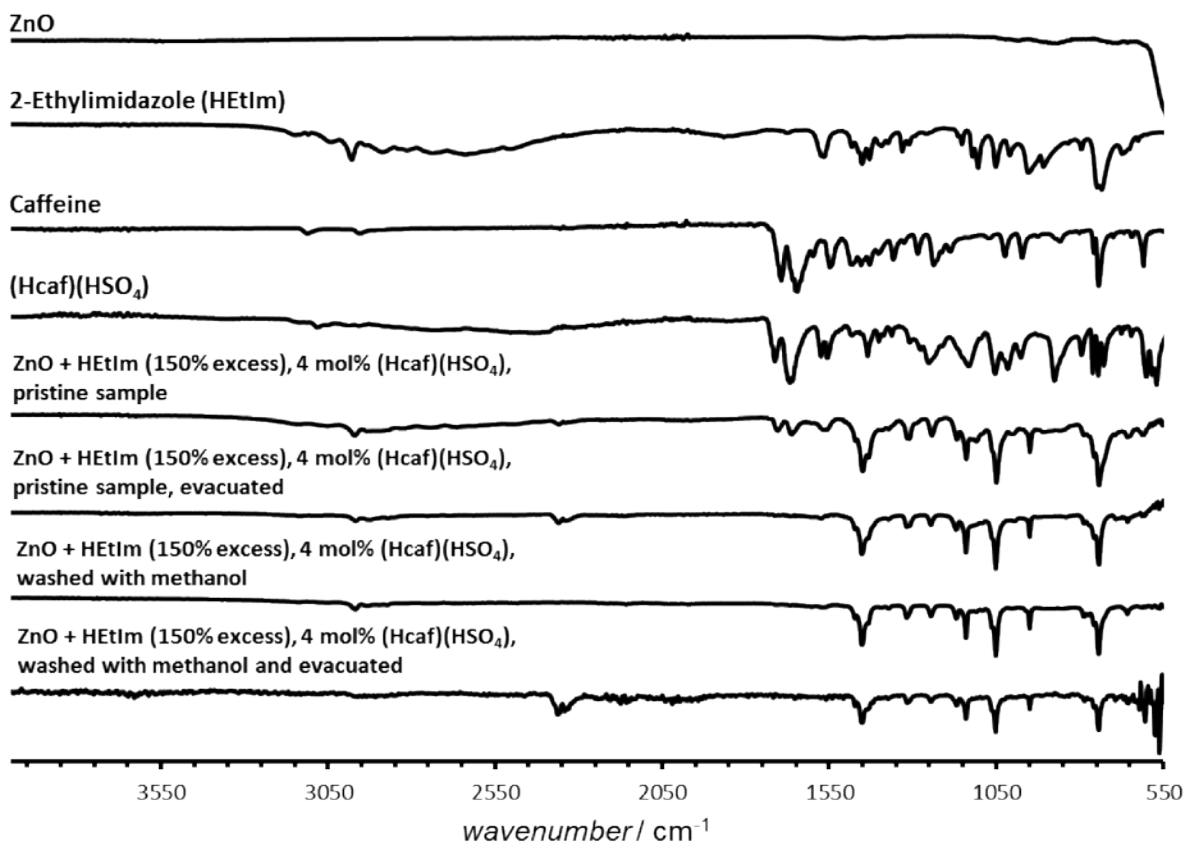
**Figure S35.** Selected FTIR-ATR spectra for reactants and products of accelerated aging reactions of ZnO and **HMeIm**, leading to the formation of the ZIF-8 structure, in the presence of 4 mol% (calculated based on ZnO) of  $(\text{H}_2\text{im})_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  as the ionic additive.



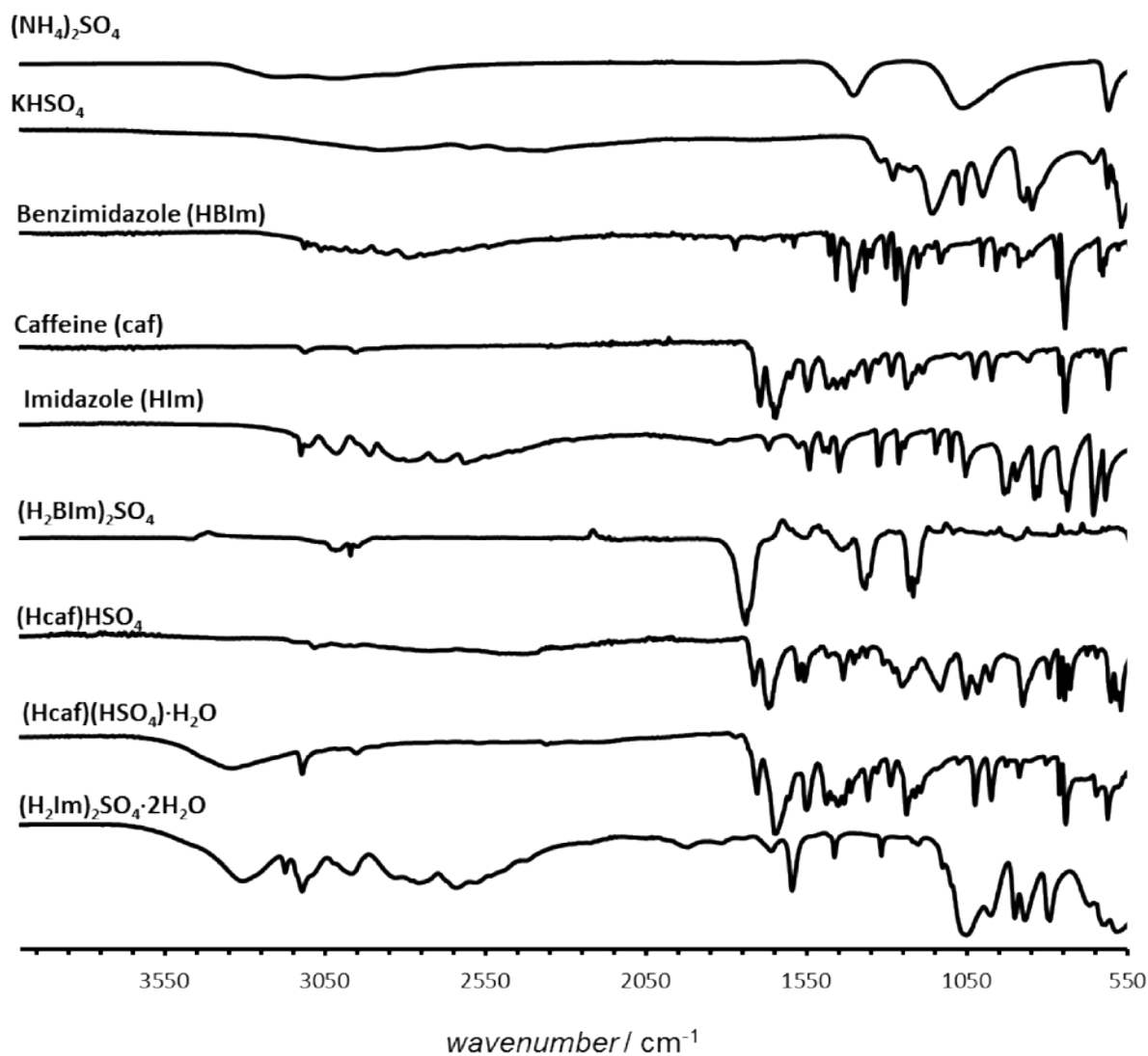
**Figure S36.** Selected FTIR-ATR spectra for reactants and products of accelerated aging reactions of ZnO and **HMeIm**, leading to the formation of the ZIF-8 structure, in the presence of 4 mol% (calculated based on ZnO) of **(Hcaf)(HSO<sub>4</sub>)** as the ionic additive.



**Figure S37.** Selected FTIR-ATR spectra for reactants and products of accelerated aging reactions of ZnO and **HMeIm**, leading to the formation of the ZIF-8 structure, in the presence of 4 mol% (calculated based on ZnO) of KHSO<sub>4</sub> as the ionic additive and 20% excess of ligand **HMeIm**.

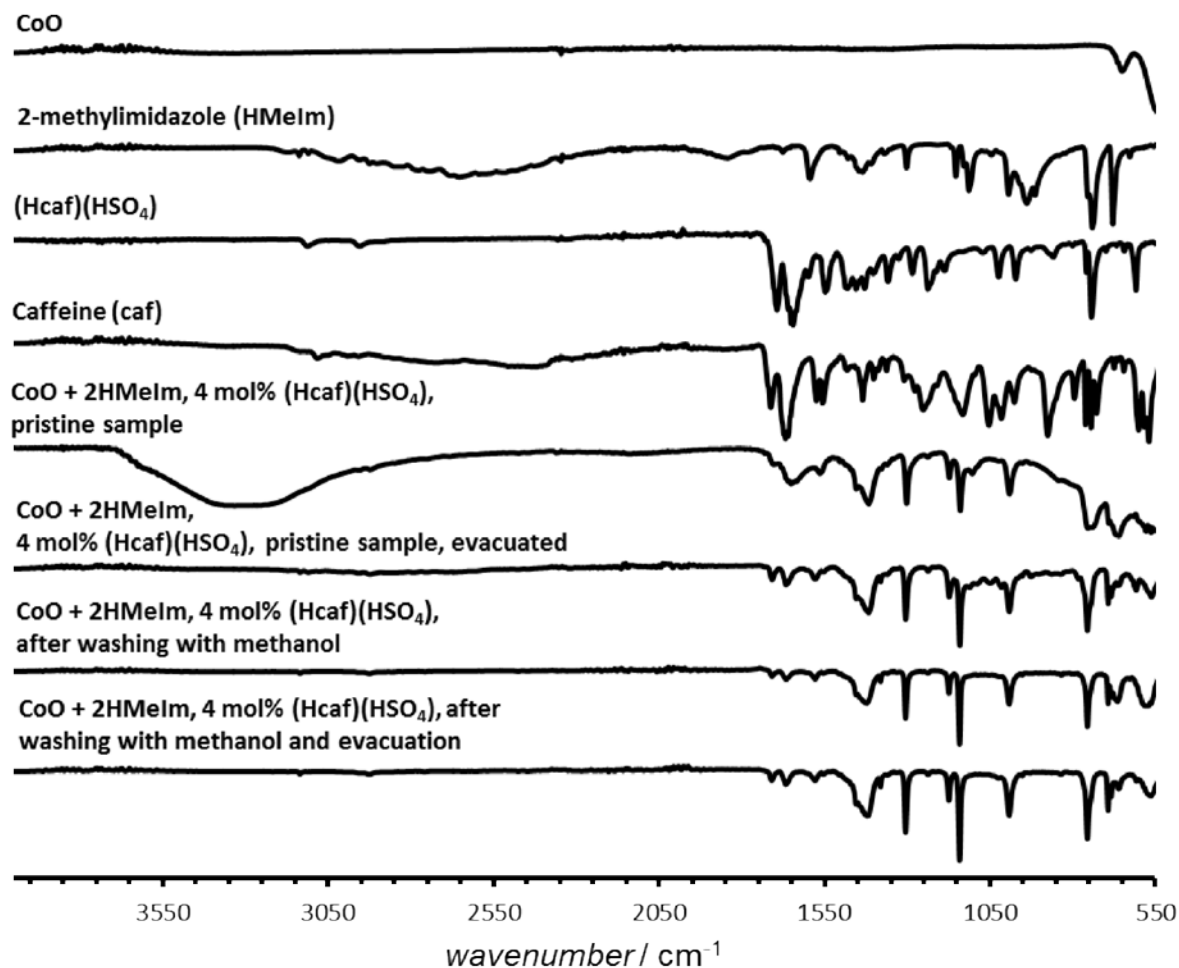


**Figure S38.** Selected FTIR-ATR spectra for reactants and products of accelerated aging reactions of ZnO and **HETIm**, leading to the formation of the RHO topology  $\text{Zn}(\text{EtIm})_2$ , in the presence of 4 mol% (calculated based on ZnO) of **(Hcaf)(HSO<sub>4</sub>)** as the ionic additive and 150% excess of ligand **HETIm**.

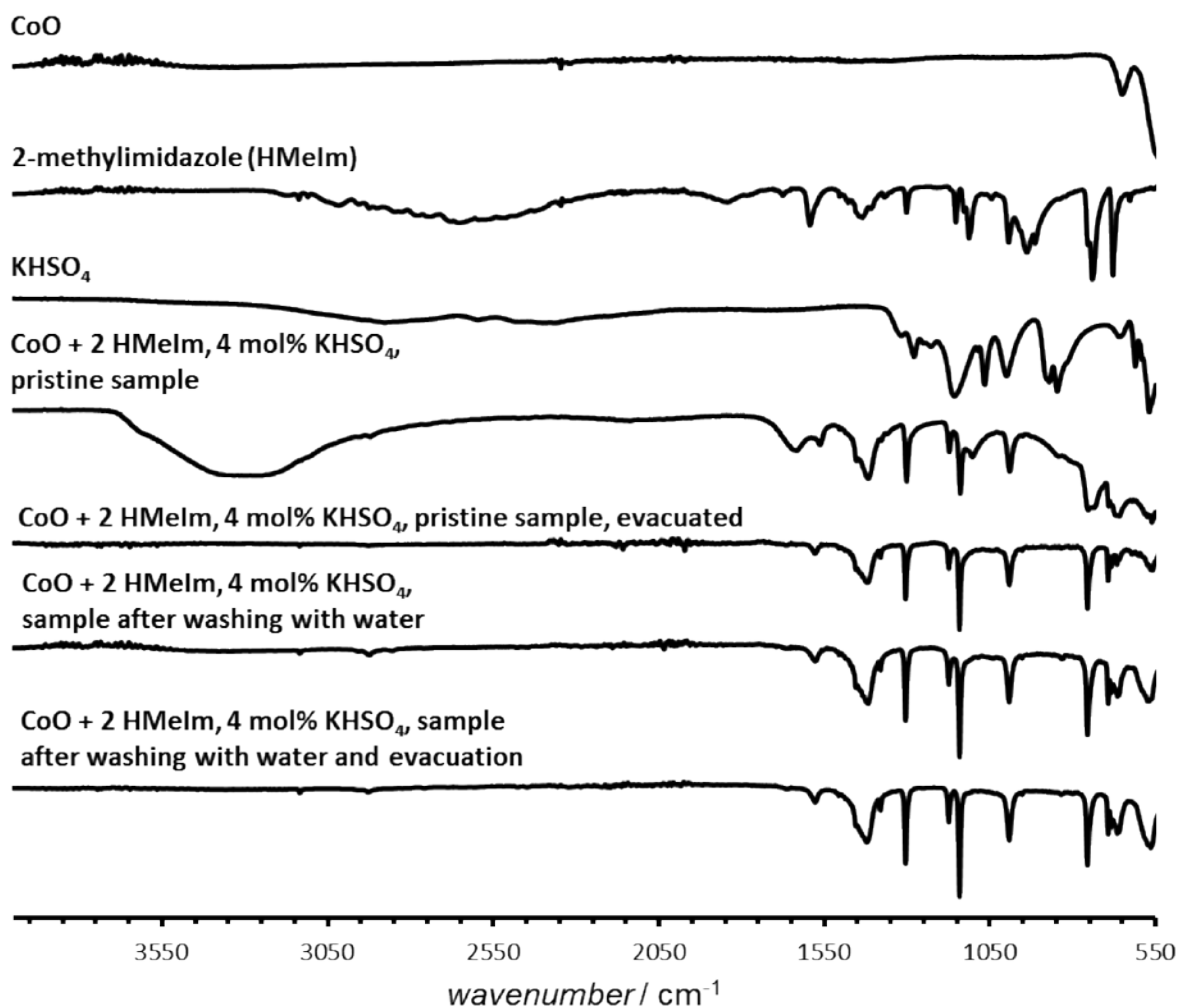


**Figure S39.** FTIR-ATR spectra for the salts used as additives in accelerated aging reactions, and for selected salt precursors.

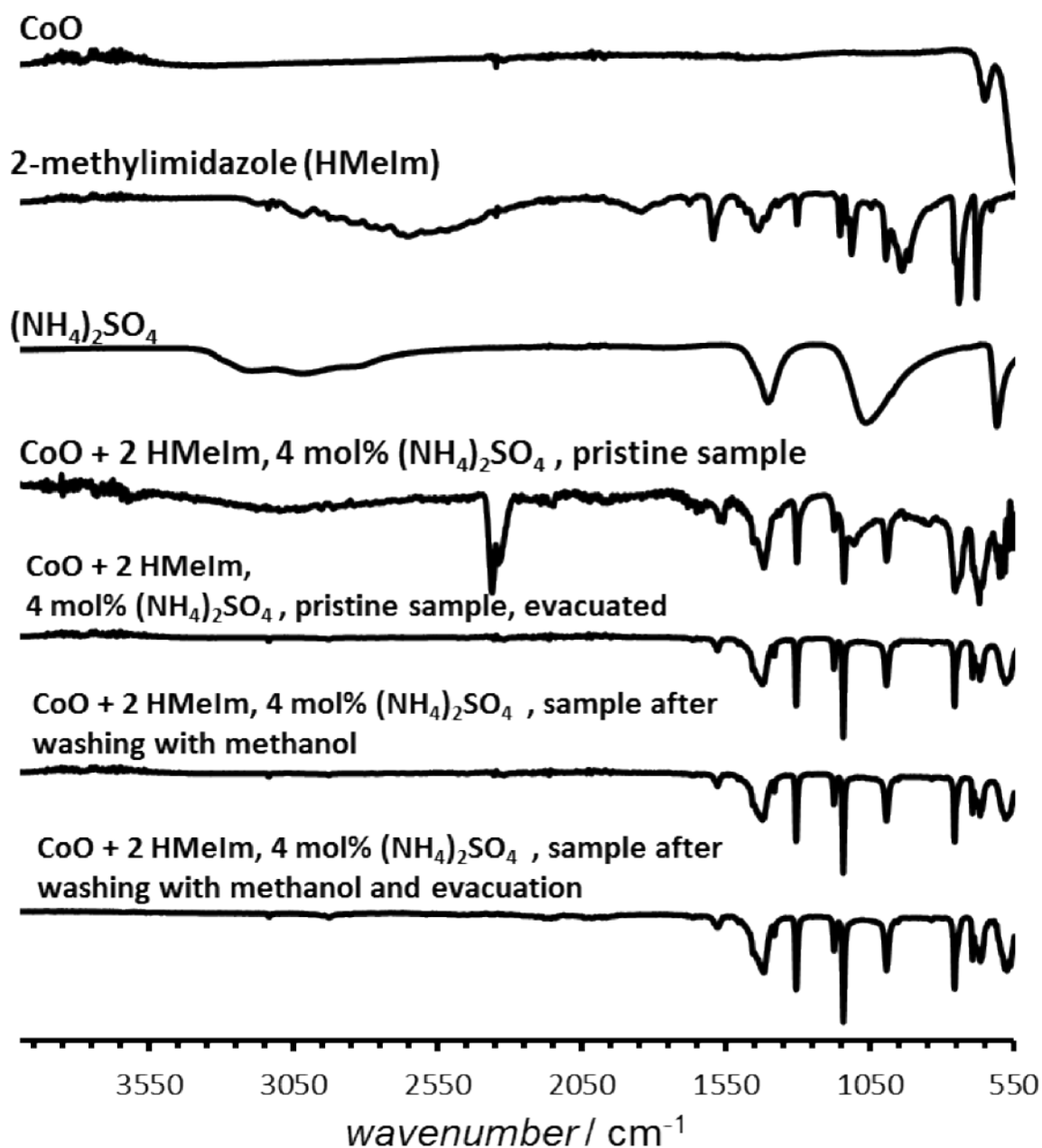




**Figure S40.** Selected FTIR-ATR spectra for reactants and products of accelerated aging reactions of CoO and **HMeIm**, leading to the formation of the ZIF-67 structure, in the presence of 4 mol% (calculated based on CoO) of **(Hcaf)(HSO<sub>4</sub>)** as the ionic additive.

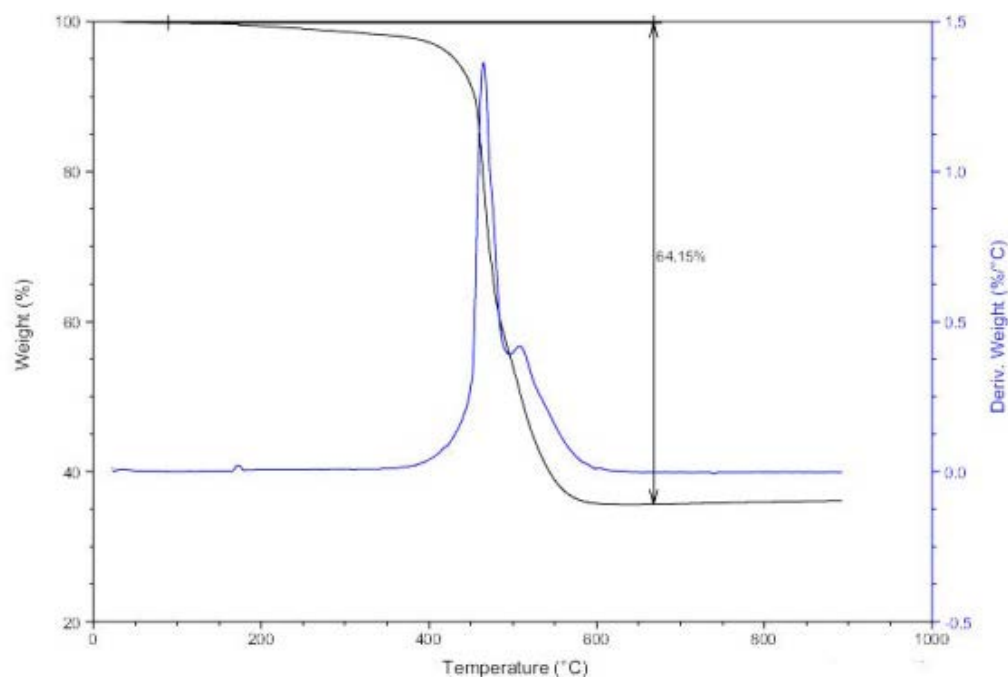


**Figure S41.** Selected FTIR-ATR spectra for reactants and products of accelerated aging reactions of CoO and **HMeIm**, leading to the formation of the ZIF-67 structure, in the presence of 4 mol% (calculated based on CoO) of KHSO<sub>4</sub> as the ionic additive.

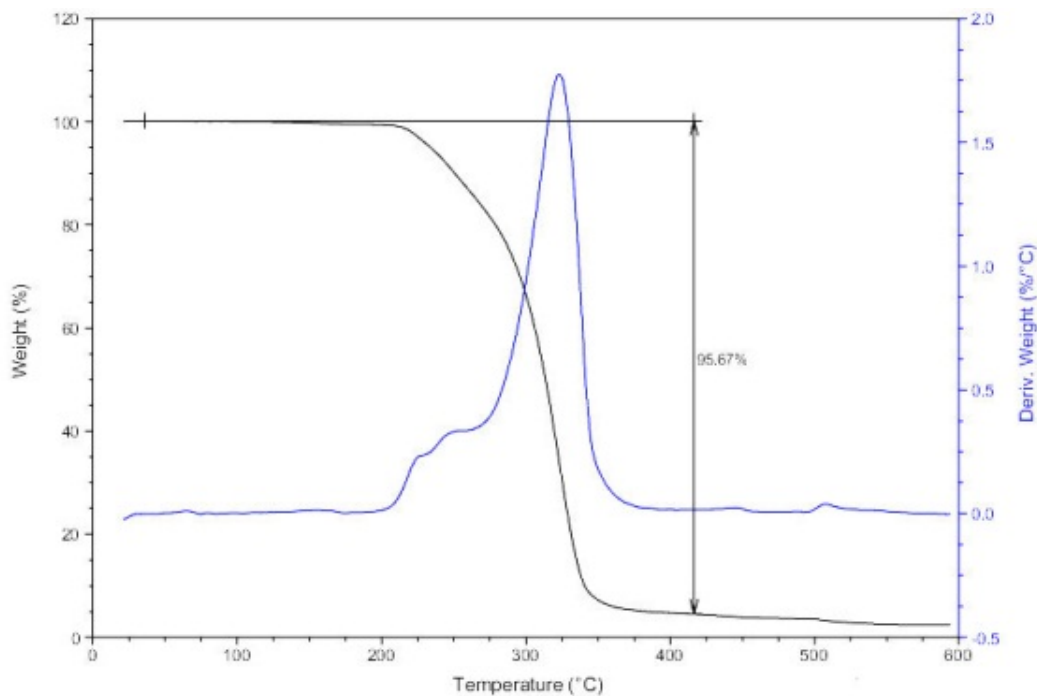


**Figure S42.** Selected FTIR-ATR spectra for reactants and products of accelerated aging reactions of CoO and **HMeIm**, leading to the formation of the ZIF-67 structure, in the presence of 4 mol% (calculated based on CoO) of  $(\text{NH}_4)_2(\text{SO}_4)$  as the ionic additive.

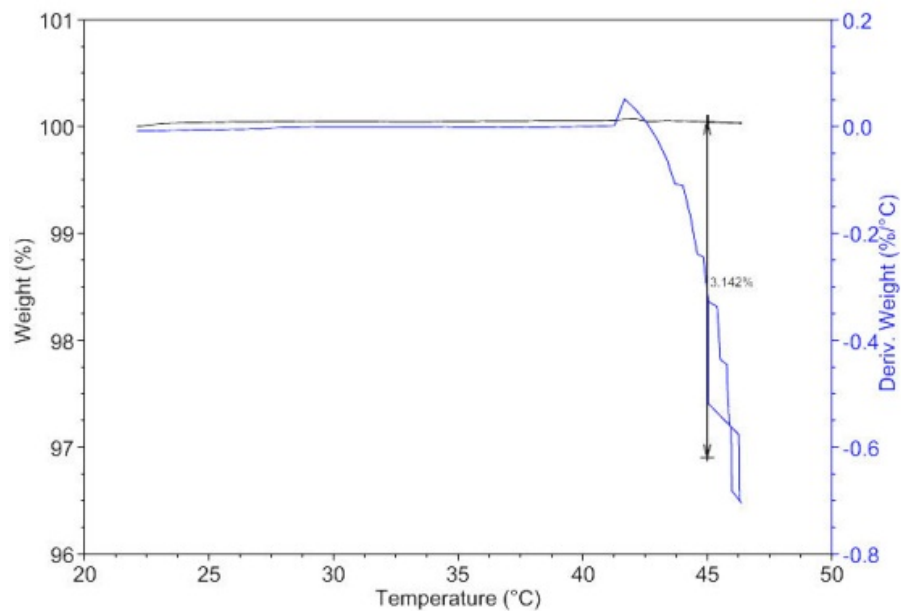
## 5. SELECTED THERMOGRAVIMETRIC ANALYSIS (TGA) DATA



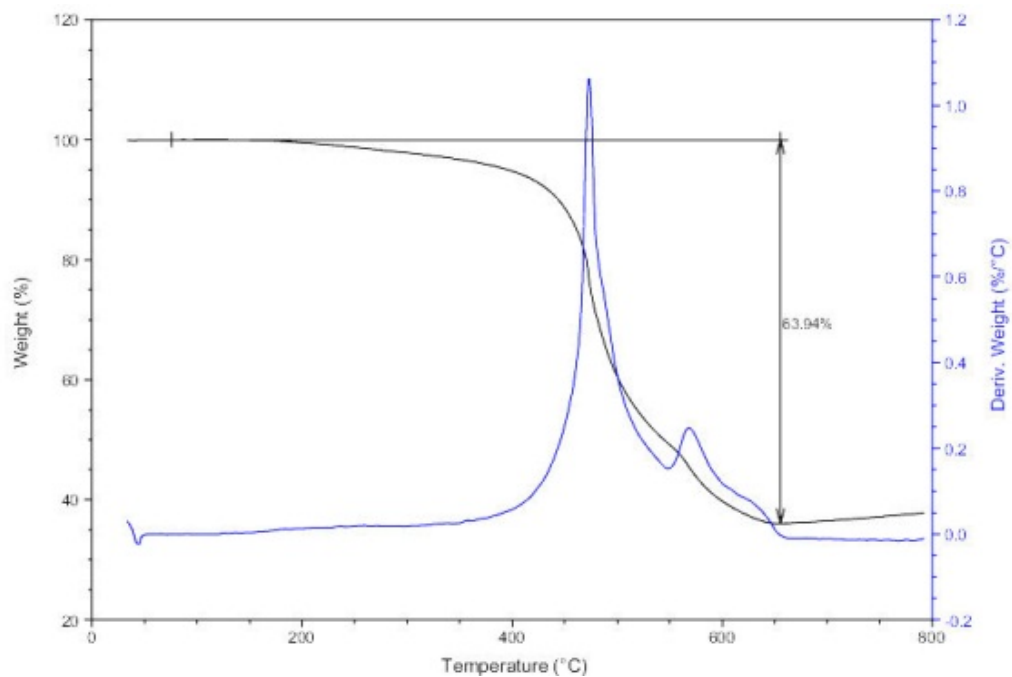
**Figure S43.** TGA thermogram for ZIF-8 sample obtained in the presence of 4 mol% (**Hcaf**)(HSO<sub>4</sub>) as the ionic additive (98% RH, 45°C), after washing and evacuation, recorded in a dynamic atmosphere of air. Theoretically expected ZnO residue: 35.8%; observed: 35.8%; calculated yield: 100%.



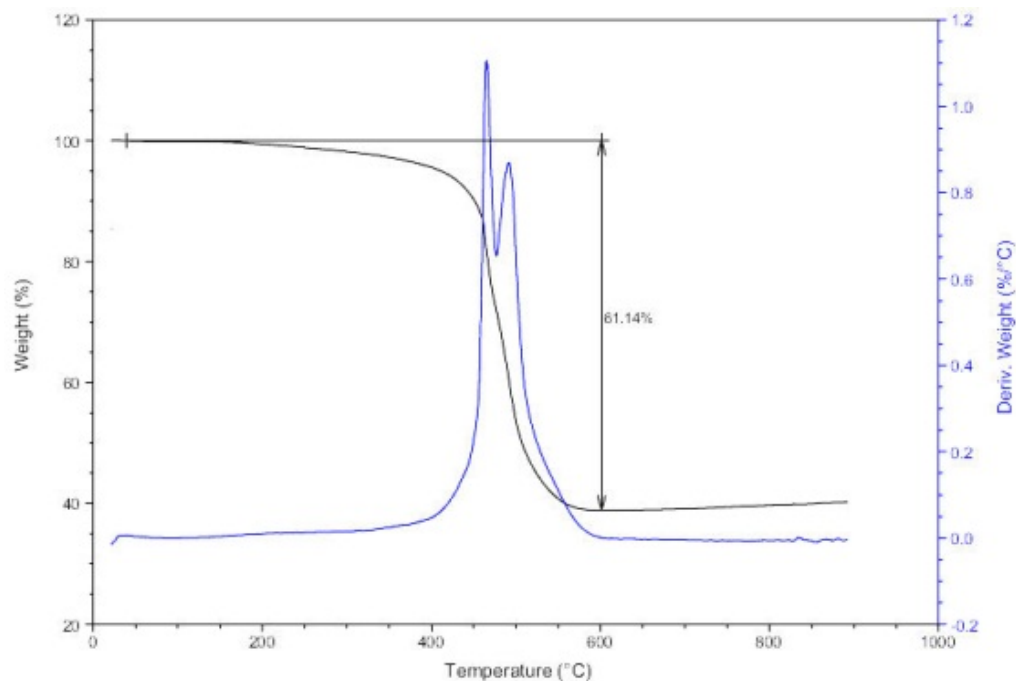
**Figure S44.** TGA thermogram for (**Hcaf**)(HSO<sub>4</sub>), recorded in a dynamic atmosphere in air. The sample does not lose weight until above 200 °C, confirming it is not a solvate.



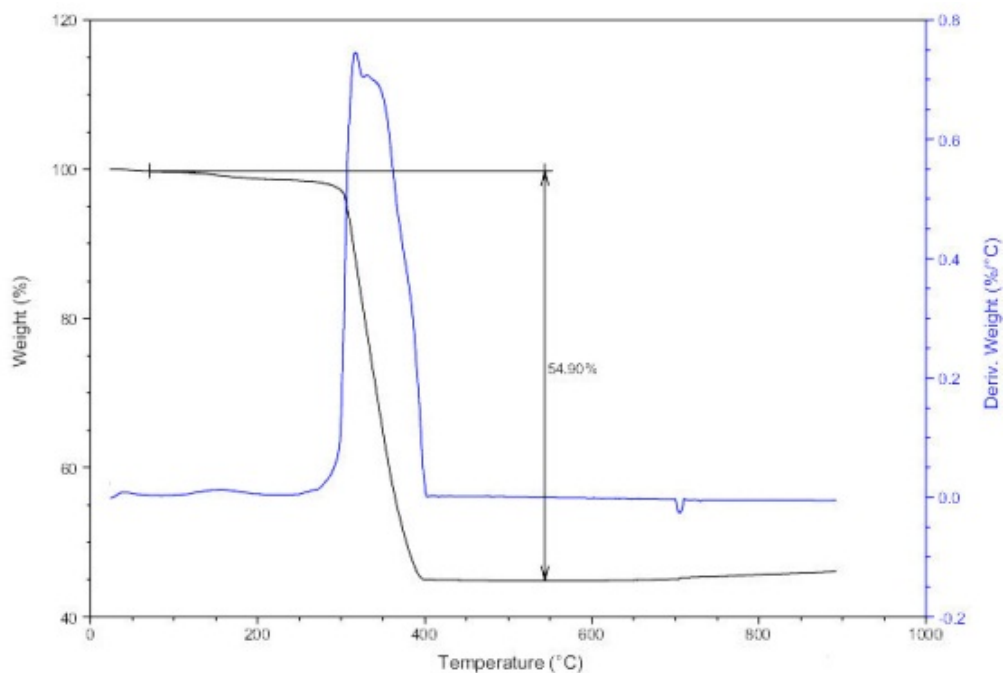
**Figure S45.** TGA thermogram of commercial **2-HMeIm**, heated at 45 °C for 14 hours in a dynamic atmosphere of nitrogen gas.



**Figure S46.** TGA thermogram for another ZIF-8 sample obtained in the presence of 4 mol% (**Hcaf**)(HSO<sub>4</sub>) as the ionic additive (98%RH, 45 °C), after washing and evacuation, recorded in a dynamic atmosphere in air. Theoretically expected ZnO residue: 35.8%; observed: 36.0%; calculated conversion: 99%.

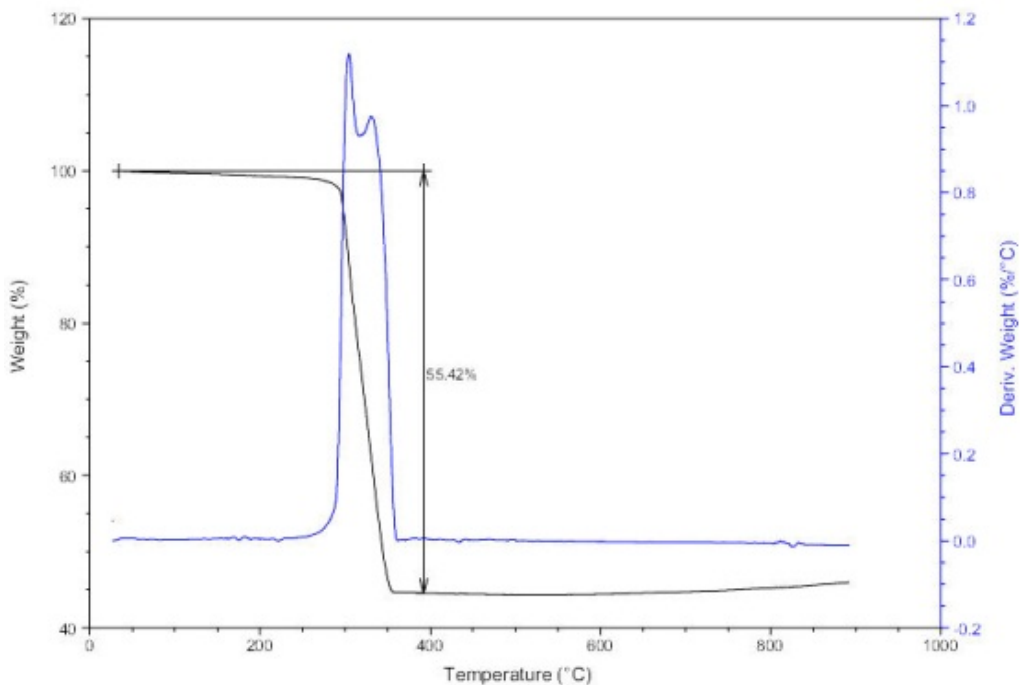


**Figure S47.** TGA thermogram for a ZIF-8 sample obtained in the presence of 4 mol%  $(\text{H}_2\text{Im})_2(\text{SO}_4) \cdot 2\text{H}_2\text{O}$  as the ionic additive (98% RH, 45 °C), after washing and evacuation, recorded in a dynamic atmosphere in air. Theoretically expected ZnO residue: 35.8%; observed: 39.0%; calculated conversion: 87%.

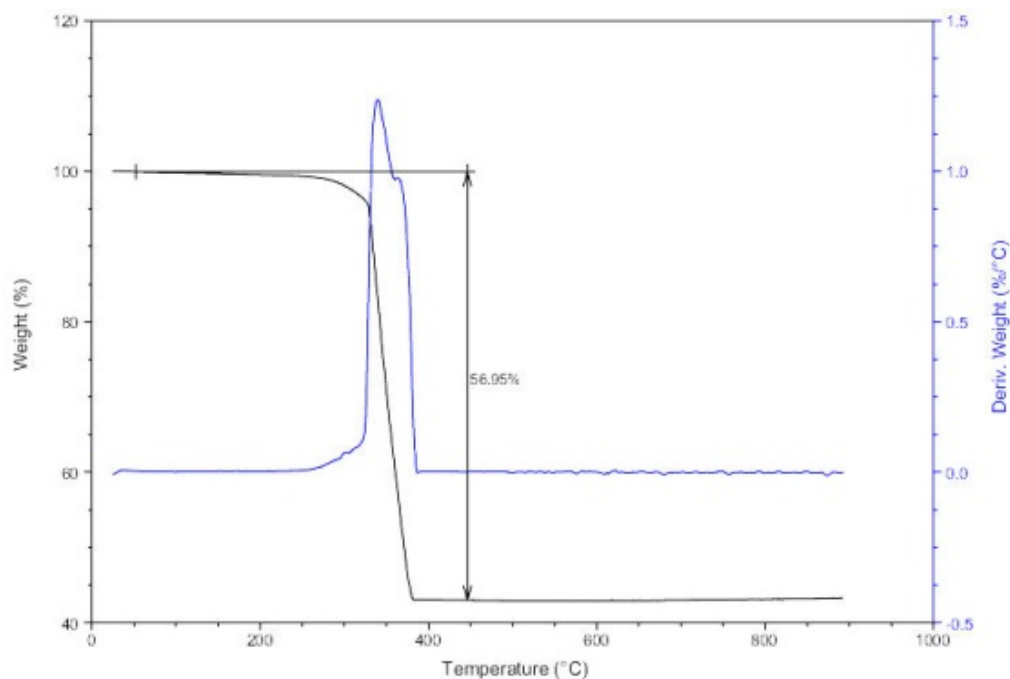


**Figure S48.** TGA thermogram for a ZIF-67 sample obtained in the presence of 4 mol%  $(\text{NH}_4)_2(\text{SO}_4)$  as the ionic additive (98% RH, 45 °C), after washing and evacuation, recorded in a dynamic atmosphere in air. Theoretically expected  $\text{Co}_3\text{O}_4$  residue: 36.3%; observed: 45.1%; calculated conversion: 71%. Reaction scale: 5 grams.

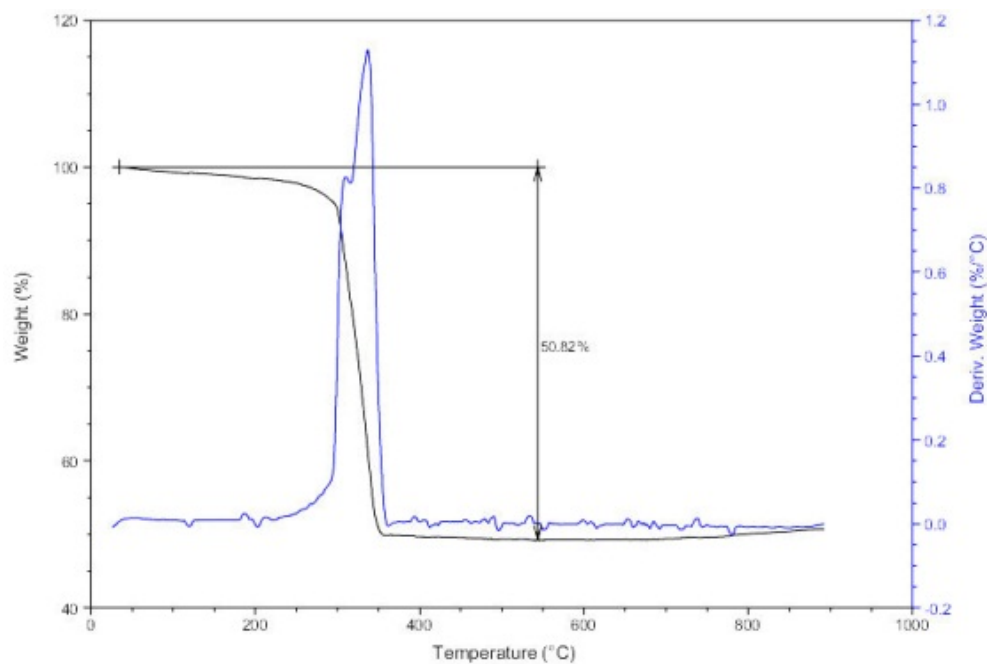




**Figure S49.** TGA thermogram for a ZIF-67 sample obtained in the presence of 4 mol% (**Hcaf**)(HSO<sub>4</sub>) as the ionic additive (98% RH, 45 °C), after washing and evacuation, recorded in a dynamic atmosphere in air. Theoretically expected Co<sub>3</sub>O<sub>4</sub> residue: 36.3%; observed: 44.6%; calculated conversion: 72%.

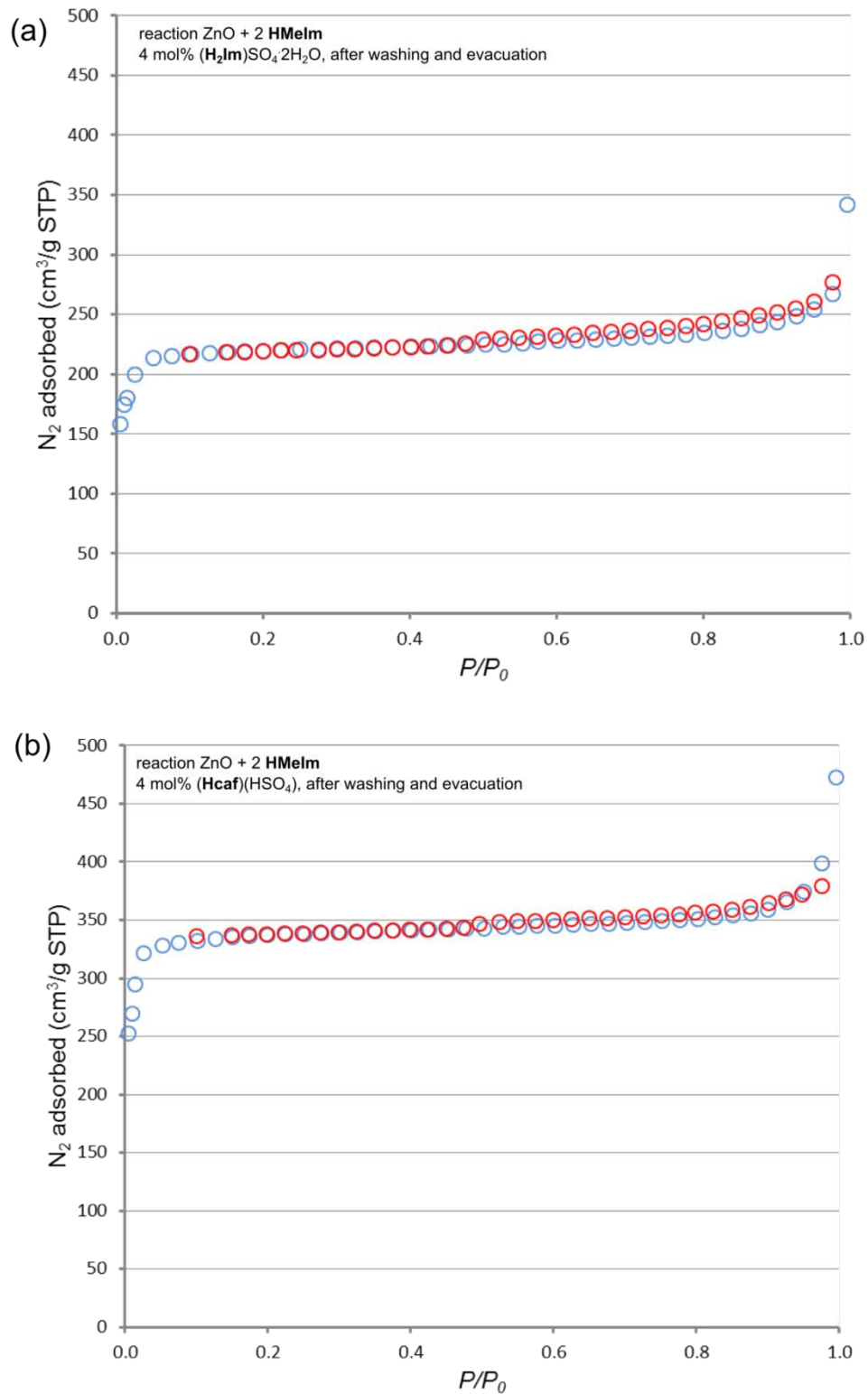


**Figure S50.** TGA thermogram for a ZIF-67 sample obtained in the presence of 4 mol% (**Hcaf**)(HSO<sub>4</sub>) as the ionic additive and 100% RH, after washing and evacuation, recorded in a dynamic atmosphere in air. Theoretically expected Co<sub>3</sub>O<sub>4</sub> residue: 36.3%; observed: 43.0%; calculated conversion: 77%.

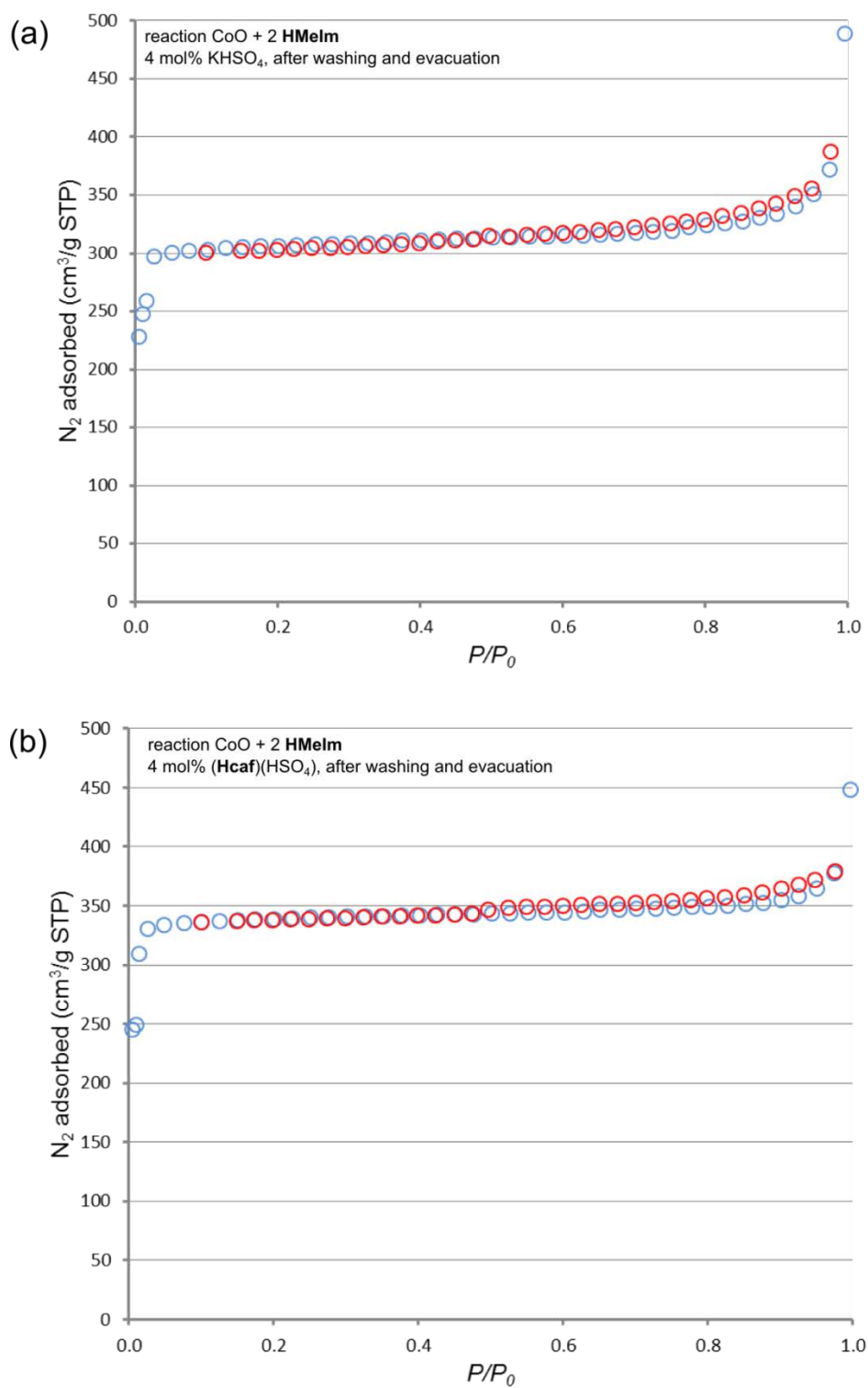


**Figure S51.** TGA thermogram for a ZIF-67 sample obtained in the presence of 4 mol%  $\text{KHSO}_4$  as the ionic additive, after washing and evacuation, recorded in a dynamic atmosphere in air. Theoretically expected  $\text{Co}_3\text{O}_4$  residue: 36.3%; observed: 49.1%; calculated conversion: 61%.

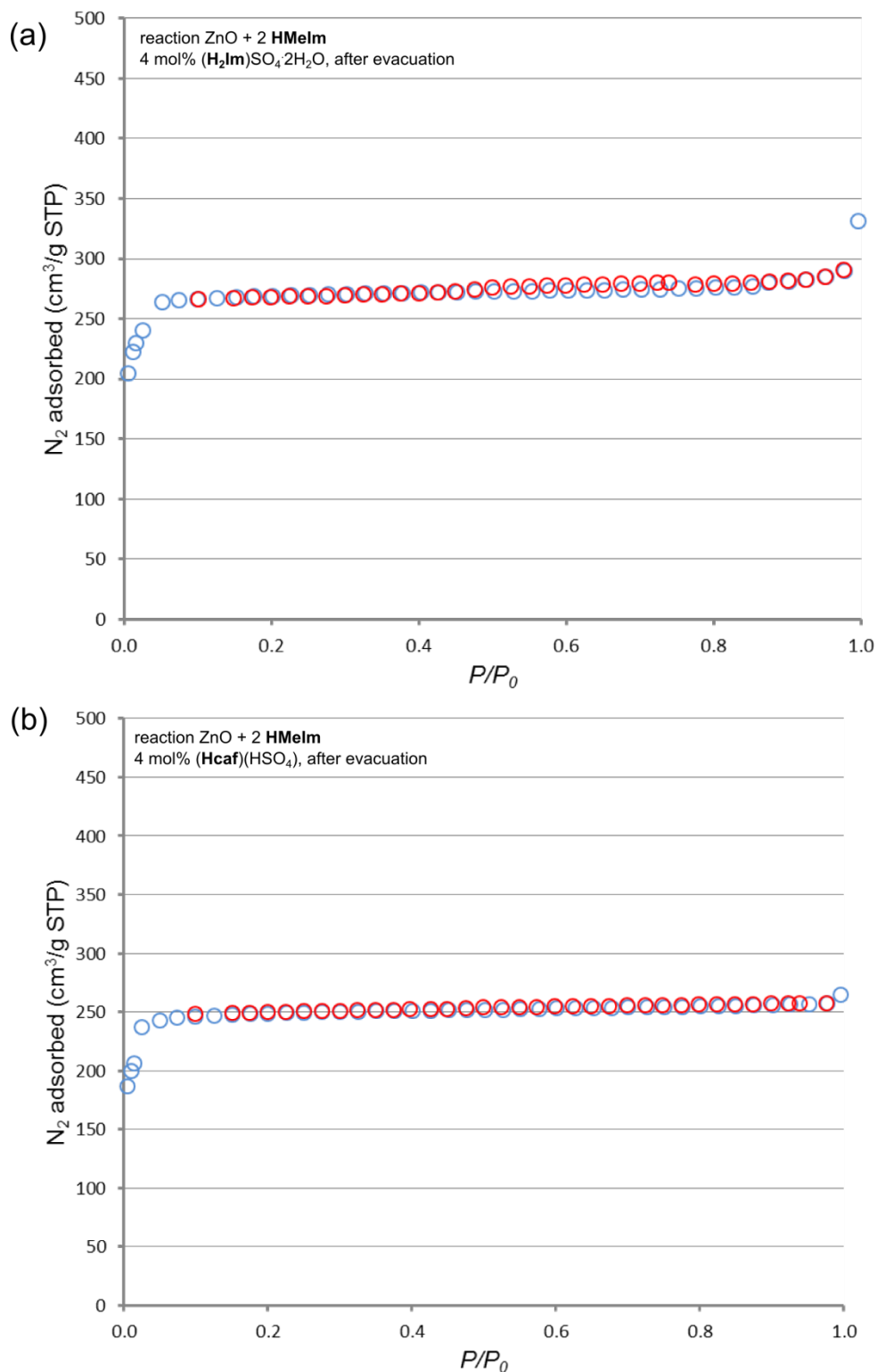
## 6. SELECTED GAS SORPTION ANALYSIS DATA



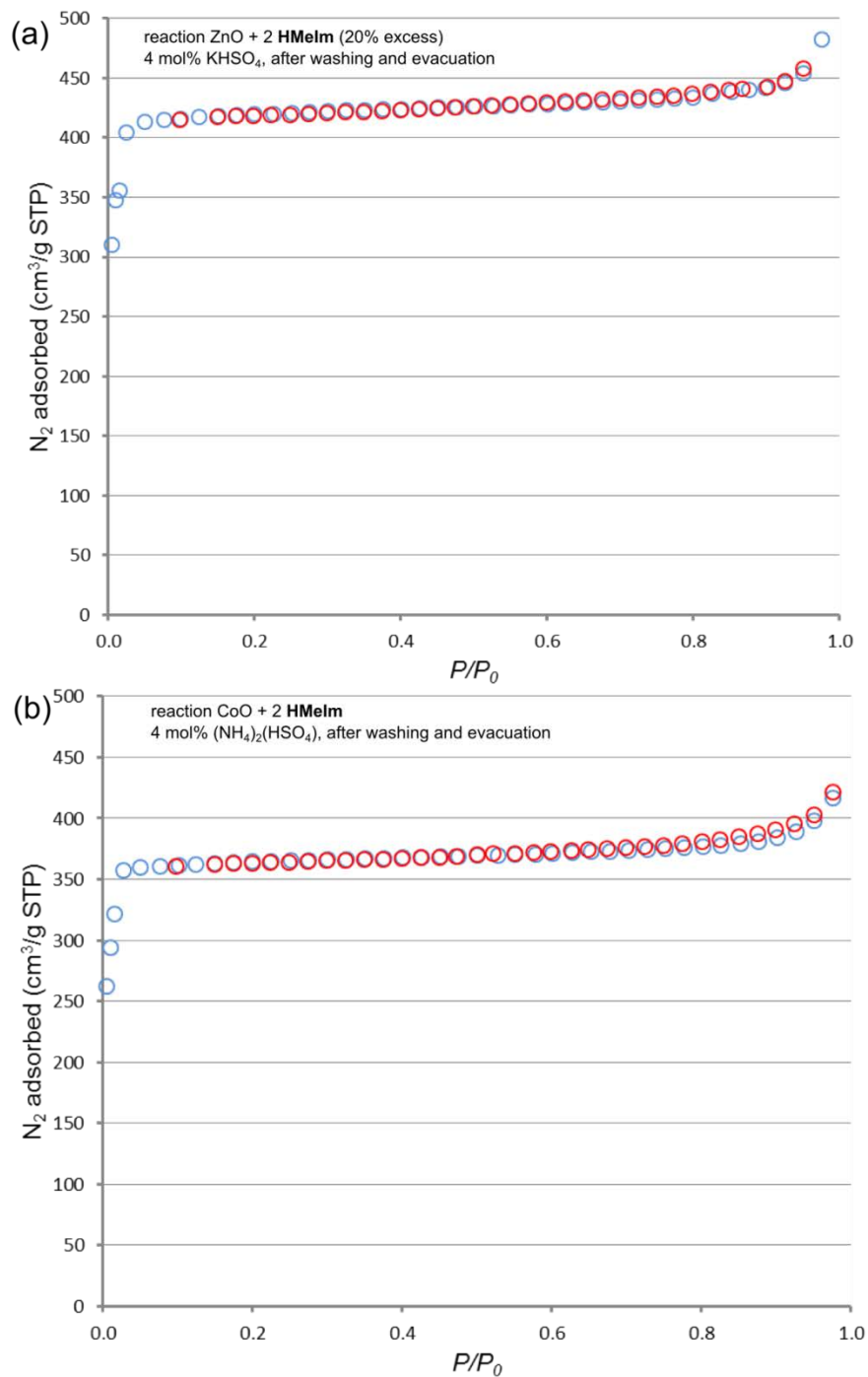
**Figure S52.** Nitrogen adsorption isotherms for ZIF-8 samples obtained by accelerated aging of ZnO and HMeIm using: (a)  $(\text{H}_2\text{Im})_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  or (b)  $(\text{Hcaf})(\text{HSO}_4)$  ionic additives, after washing and evacuation.



**Figure S53.** Nitrogen adsorption isotherms for ZIF-67 samples obtained by accelerated aging of CoO and HMeIm using: (a)  $\text{KHSO}_4$  or (b)  $(\text{Hcaf})(\text{HSO}_4)$  ionic additives, after washing and evacuation.

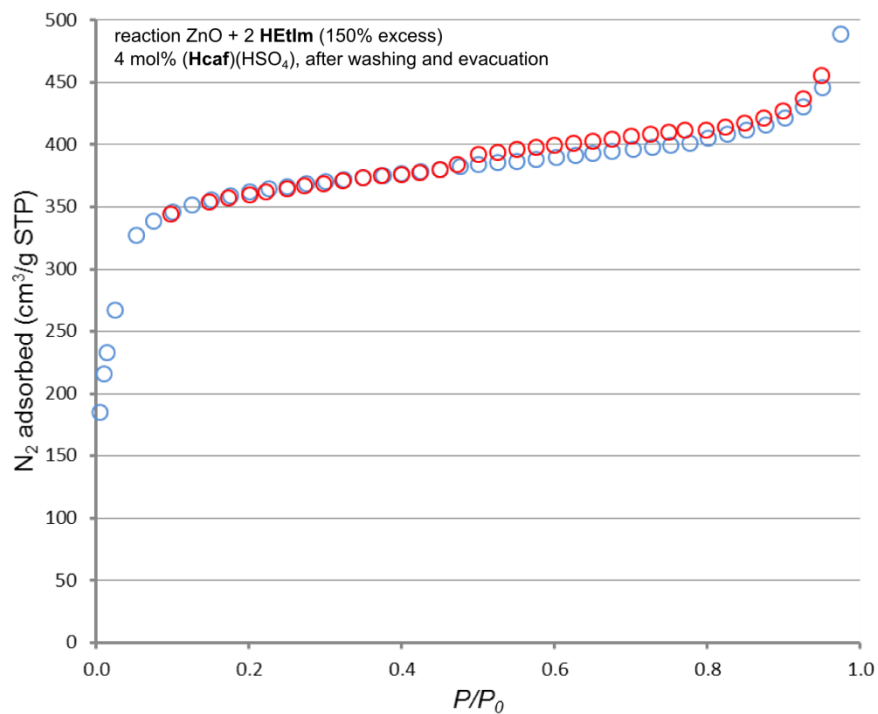


**Figure S54.** Nitrogen adsorption isotherms for ZIF-8 samples obtained by accelerated aging of ZnO and **HMeIm** using: (a) (**H<sub>2</sub>Im**)<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O or (b) (**Hcaf**)(HSO<sub>4</sub>) ionic additives, after evacuation.



**Figure S55.** Nitrogen adsorption isotherms for: (a) ZIF-8 sample obtained by accelerated aging of ZnO and **HMeIm** using **(Hcaf)(HSO<sub>4</sub>)** ionic additive in the presence of 20 mol% excess **HMeIm**, after washing and evacuation and (b) ZIF-67 sample obtained by accelerated aging of CoO and **HMeIm** using  $(NH_4)_2SO_4$  ionic additive, after washing and evacuation.





**Figure S56.** Nitrogen adsorption isotherm for the zeolite RHO topology Zn(**EtIm**)<sub>2</sub> obtained by accelerated aging of ZnO and **HEtIm** using (**Hcaf**)(HSO<sub>4</sub>) ionic additive in the presence of 150 mol% excess **HEtIm**, after washing and evacuation.