Scientific Achievement
This work shows that defect formation is more thermodynamically and kinetically favorable at ZIF external surfaces versus the bulk, and that both topology and ligand functionalization impact defect formation.

Significance and Impact
The current study provides a detailed mechanism for the reaction of ZIFs with sulfurous and sulfuric acids, of which the latter serves as a catalyst in potential degradation reactions of ZIFs. Information about the adsorption strength is provided for a range of acid gases to defective ZIF structures, which can inform potential strategies to regenerate ZIFs and/or achieve defect engineering in these materials.

Research Details
– Dispersion-corrected density functional theory calculations were used to investigate the chemical stability of bulk ZIFs and their external surfaces under conditions of acid-gas exposure.
– ZIF-2 and ZIF-8 were used as prototypical materials for our calculations. These two ZIFs differ in their pore sizes, topologies, and ligand functionalization.
Potential degradation mechanisms and reaction energies for ZIFs with a Brønsted and Lewis acid

Degradation in ZIFs begins with Zn–N bond cleavage, which may result in point defects such as dangling linkers (DL), linker vacancies (LV), and metal cation vacancies.

DLs are thought to emerge first, followed by the formation of other defects.

Studied the interactions of defect-free bulk structures, external surfaces, and point defects in ZIF pores with acid gases and water.

\[ \Delta E_{\text{rxn,DL}} = E_{\text{ZIF,DL}} - E_{\text{ZIF}} - E_{\text{mol}} \]

\[ \Delta E_{\text{rxn,LV}} = E_{\text{ZIF+LV}} + E_{\text{HL}} - E_{\text{ZIF}} - 2E_{\text{H}_2\text{O}} \]

\[ \Delta E_{\text{ads}} = E_{\text{mol+ZIF}} - E_{\text{mol}} - E_{\text{ZIF}} \]

L = organic imidazolate ligand

HL = protonated organic imidazolate ligand

HX = Brønsted gas molecules

X = Lewis acid gas molecules

Acid-induced dangling linker formation reactions in bulk ZIF

Formation of a linker vacancy by two water molecules

<table>
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<tr>
<th>Reactant</th>
<th>pKₐ</th>
<th>ΔE⁻⁰</th>
<th>ΔE⁻¹</th>
<th>ΔE⁻²</th>
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<tr>
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<td>H₂O</td>
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<td>-27.0</td>
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<td>Lewis acid</td>
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Stability as a function of ZIF topology and ligand species

Linker vacancy formation energies in the pores of bulk ZIF polymorphs with various topologies
- Two sets of ZIF polymorphs
  - Zn(mIM)$_2$ (ZIF-8)
  - Zn(IM)$_2$ (ZIF-2)
- Eight topologies
- Stability determined by reaction energies linker vacancy (LV) formation by two water molecules replacing a ligand
  
Zn(mIM)$_2$ materials have higher reaction energy than Zn(IM)$_2$ materials
- Possibly from larger steric bulk of the mIM ligands somewhat protects the Zn metal centers from attack by water

Cannot conclude that changes in topology or in the ligand dominates
Energy profiles and thermodynamic cycle for a linker vacancy formation in ZIF-8 reacting with H$_2$SO$_3$, H$_2$SO$_4$, and H$_2$O

The presence of even trace amounts of H$_2$SO$_4$ with SO$_2$/H$_2$SO$_3$ opens a low-barrier catalytic pathway to degradation

Reaction Step I
- Adsorption of H$_2$SO$_x$ molecule in pore
- Formation of a dangling linker (DL)

Reaction Step II
- Adsorption of H$_2$O molecule in pore
- Formation of linker vacancy (LV)

Reactions between ZIF-8 and H$_2$SO$_3$/H$_2$O in the presence of H$_2$SO$_4$
- Steps to recover a sulfuric acid from a defect formed by H$_2$SO$_4$/H$_2$O
  - Adsorption of a H$_2$SO$_3$
  - Exchange of its HSO$_3^-$ with the HSO$_4^-$ ion of the defect
  - Regenerate H$_2$SO$_4$ molecule
Dangling linker formation reaction energies in the pore of bulk ZIFs versus their surfaces for various acid gases

- Bulk and surface ZIF-8 are more thermodynamically and kinetically stable than ZIF-2 based on reactions with all the studied acid gases
  - ZIF stability governed by topology and ligand functionalization
- Surfaces are more reactive than bulk structures for both ZIF-2 and ZIF-8
  - Surfaces are more flexible than the bulk and so more prone to make steric accommodation for the defect deformation