Facet-Specific Stability of ZIF-8 in the Presence of Acid Gases Dissolved in Aqueous Solutions

Scientific Achievement

ZIF-8 metal-organic frameworks were examined for stability in the presence of mild acidic conditions. It was found that material stability is controlled by the exposed surface facets.

Significance and Impact

This study represents the first comprehensive investigation of differences between exposed surface facets of a MOF and provides guidelines for synthesizing sulfur resistant ZIFs.

Research Details

- ZIF-8 particles were synthesized to yield either \{110\} rhombic dodecahedra (RD) facets or \{100\} truncated cubes.
- Electron microscopy, BET surface area, XPS, FTIR, and diffusion studies were performed to characterize differences in stability between exposed surface facets after exposure to aqueous SO\textsubscript{2} solutions.
- Studies revealed the \{110\} RD facet was more susceptible to degradation; it is hypothesized that the mechanism for degradation follows a shrinking-core model, with surface imidazolates being replaced by hydroxyls.
- Computational investigations support this degradation mechanism and suggest that the reaction is more favorable on the \{110\} facet than the \{100\} facet due to steric constraints.
Particles exposing a single facet can be synthesized using crystal engineering techniques.

The surfaces of (100)-terminated cubes appear more stable than the surfaces of (110)-terminated RD cubes as synthesized, after 3 days, and after 14 days.
Bulk textural properties are not significantly affected, suggesting a shrinking-core model of degradation.
XPS studies suggest that imidazole is removed from the surface region and is replaced by hydroxyl.
IR studies confirm formation of hydroxyl and sulfite species, likely on the external surfaces.

Proposed sulfite-assisted degradation reactions at ZIF-8 surfaces. Imidazole is removed from the framework, and is replaced by surface sulfites or hydroxyls.