

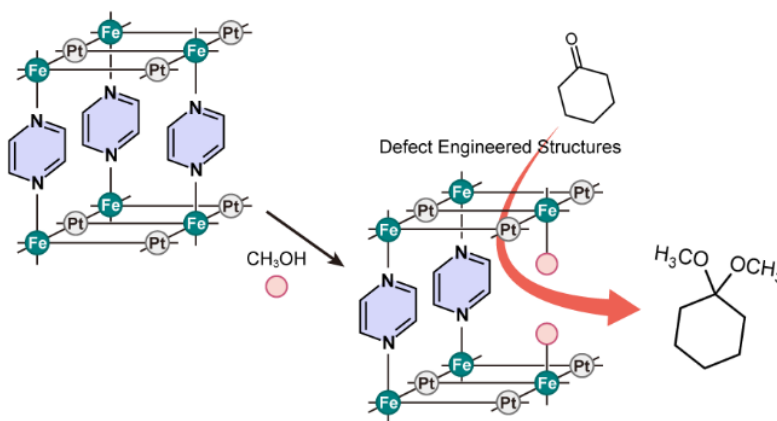
Defect Formation in Three-Dimensional Hofmann-Type Coordination Polymers

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We report a systematic investigation of post-synthetic defect formation in Hofmann-type coordination polymers $M(pz)[M'(CN)_4]$ ($M = Fe^{2+}, Co^{2+}, Ni^{2+}$; $M' = Pd^{2+}, Pt^{2+}$; $pz = \text{pyrazine}$). These compounds readily undergo selective ligand exchange at the pyrazine site when immersed in methanol (MeOH) at ambient temperature. The ligand exchange changes the chemical formula to $M(pz)_{1-x}(MeOH)_{2x}[M'(CN)_4]$ ($0 < x < 0.3$), affording defective coordination environment around the M ions. The defect concentration is highly dependent on the combination of the metal ions and solvent species, reaching the defect concentration of ca. 30% ($x \sim 0.3$) at maximum. The magnetic state of one such coordination polymer gives an additional control of the defect formation, making the compound less susceptible to the ligand exchange at the low-spin state.

Structures that form the defects at high concentration function as catalysts and promote an acetalization reaction heterogeneously by providing Lewis acidic sites. The solvent-dependent character of the defect formation can be used to control the catalytic activity of the active compounds, demonstrating a facile defect engineering for functionalizing solid materials.¹⁾



References

- 1) D. Umeyama, A. Takai, K. Sonobe, *Inorg. Chem.* **2022**, *61*, 1697-1703.