Previews

Robust Mesoporous Zr-MOF with Pd Nanoparticles for Formic-Acid-Based Chemical Hydrogen Storage

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Formic acid is a compelling chemical storage platform for hydrogen gas, but the lack of an efficient dehydrogenation catalyst is preventing its commercial use. In this issue of *Matter*, Wang et al. report a fine-tuned zirconium metal-organic framework with palladium nanoparticles that effectively dehydrogenates formic acid without degradation.

Mesoporosity in solid structures with pores between the diameters of 2–50 nm offers diverse applications including adsorption, catalysis, energy storage, and conversion.[1] The scope of materials reach far and beyond, with the likes of activated carbon, silica, zeolites, and most recently metal-organic frameworks (MOFs). Each class of mesoporous materials have advantages over the others but it's not common to have many features in one. The competition between stability and functionality is steep, where a resilient structure often needs to be devoid of reactive sites.

MOFs offer limitless tunability with interchangeable metal nodes and ligands, and mesoporous MOFs are not uncommon. The challenge is usually the stability because a large pore also means more exposure to reactive substrates and less structural integrity because of the sizeable voids. Zirconium (Zr) oxide nodes are excellent overcoming this challenge by providing a 12-coordinate secondary building unit (SBU),[2] but the higher coordination also means limits for the pore size diameters. It is in this precise point that Wang and co-workers made their mark by assembling alternate 6 and 12 coordinate Zr-SBUs, hence expanding the pore size to the mesoporous regime without sacrificing structural robustness.[3] The resulting MIPs (Materials of the Insti-

tute of Porous Materials of Paris) feature 2.5–2.7 nm pores while preserving resistance to strong acids (even aqua regia!) and bases (up to pH = 12).

In energy storage, the porous materials are primarily considered for physical storage, where there is no covalent interaction between the fuel and the host. Recent developments in MOFs and porous polymers have brought exciting new fronts, particularly the flexible framework structures. For example, we recently reported[4] flexible alkane-linked porous aromatic polymers that expand by the pressurized methane and yield record high capacities in adsorbed natural gas (ANG) technology. But the requirements for high pressures and sealed/cooled tanks are not always attractive for widespread application, particularly when long term storage in remote locations is desired.

In hydrogen storage, physical storage becomes less feasible than methane for the same reasons and also because of the additional volatility from its smaller molecular dimensions. This is where chemical energy storage comes in to the rescue. Among the contenders, formic acid is an emerging host for reversible hydrogen storage. It is because formic acid is a very kinetically stable liquid at room temperature and contains 4.4 wt% hydrogen, fulfilling the hydrogen storage

capacity targets by the United States Department of Energy (DOE).[5] The dehydrogenation (DH) process of formic acid to H_2 and CO_2 is thermodynamically quite favorable by $\Delta G = -32.9$ kJ mol^{-1}, and it shows 100% atom-efficient catalytic storage. Moreover, formic acid can be used as an important intermediate, by-product and product in the chemical industry as well as biomass processes.[6]

The mesoporous MIPs have the porosity and stability to handle formic acid transformations but not the right chemistry for an effective catalytic turn over. Even if a proper catalyst was introduced, the loading and activity don't always go hand in hand. The pore blocking, for example, is a common cause for failure. Undeterred of limitations, the team went ahead with loading palladium precursors into the mesopores and reduced them *in situ* to provide rattle structures. Indeed, the rattle structures are quite effective,[7] where a nanoparticle (NP) is locked inside the pore by being larger than the pore openings but not fully occupying the pore allowing safe passage of substrates and products.

The design for MIP-based formic acid catalysts, therefore, included a nontoxic Zr-SBU and isophthalic acid (IPA) linkers with well-ordered meso channels. The archetypal MIP, MIP-206, was prepared by heating $ZrCl_4$, isophthalic acid, and

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https://doi.org/10.1016/j.matt.2020.12.011
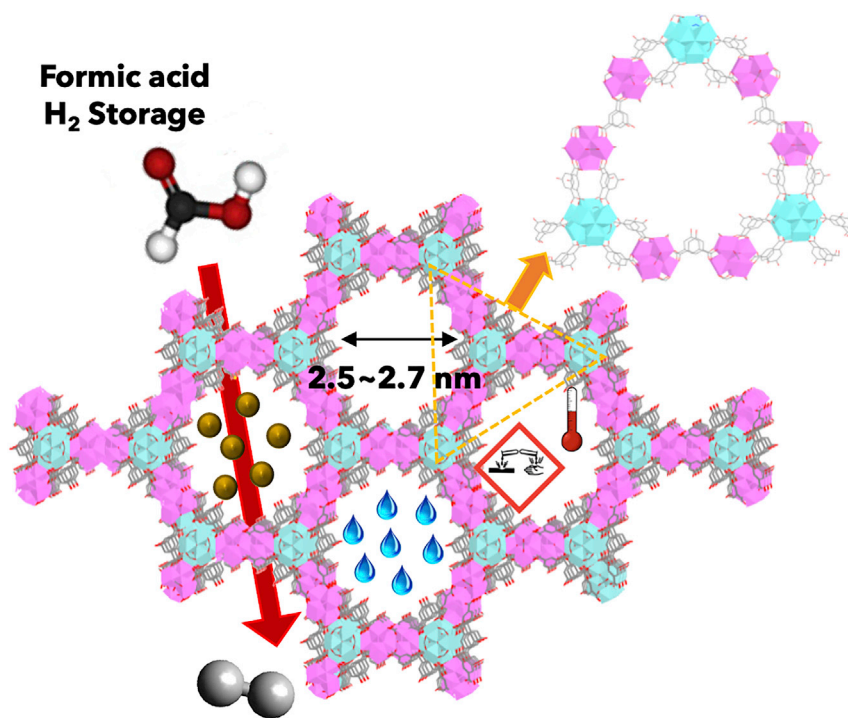
Figure 1. Formic Acid Dehydrogenation by Pd Nanoparticles Loaded Mesoporous Metal-Organic Frameworks

Porous zirconium (Zr) isophthalate crystals with 6- and 12-coordinate Zr-oxo nodes allow mesoporosity, a feature not normally available in pure 12-coordinate structures. Mesoporous MIP-206 with encapsulated rattle-like Pd nanoparticles provide exceptional activity in formic acid dehydrogenation while being stable in extreme conditions like aqua regia.

formic acid under solvothermal conditions. This one step and remarkably simple preparation also aids in scale-up and linker variation with substituted IPA linkers as well as the multivariate versions of MIP-206 series based on mixed linkers.

The exact structure of MIP-206 (Figure 1) was judiciously evaluated by a computational reverse topological construction method combined with synchrotron X-ray diffraction single-crystal analysis and high-resolution powder X-ray diffraction (PXRD) data. Simulated structure of MIP-206 contains molecular formula of $[Zr_{12}(\mu_3\text{-O})_8(\mu_3\text{-OH})_8(\mu_2\text{-OH})_6(\text{formate})_6]$ $[Zr_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{formate})_4]_3 (IPA)_{18}$ and crystallized in a hexagonal P-62C space group with unit cell parameters of a = b = 33.7520(5) Å, c = 21.4610(3) Å, V = 21172.86(5) Å^3. Here, the Zr oxo-clusters (Zr_6 and Zr_{12} connectors) act as SBUs and

form the unique angle in between the two carboxylate groups of the IPA linker. In this structure, two types of homometallic Zr_{12} and Zr_6 oxo-clusters are present, which connected with six pairs of IPA molecules. In the close examination, each Zr_6 oxo-cluster present at triangle vertex position and a pair of IPA linkers bridge in between the closest Zr_6 oxo-cluster and further connect with the neighboring units (Figure 1). Overall, meso channel of ca. 2.6 nm was formed by three Zr_{12} oxo-clusters and six Zr_6 oxo clusters. The authors called this arrangement homometallic-multicluster-dot (HMD) strategy. In the two-dimensional (2D) layers, an additional small triangle cavity of ca 7 Å observed in between Zr_6 oxo-clusters and the IPA pairs. However, ABAB stacking along C-axis results in an accessible meso-channels with anchoring of functional groups of IPA. MIP-206 series exhibit excellent structural sustainability even varying electron

donating/withdrawing groups, halogens, and heteroatoms substitutions of IPA although the slight variation of PXRD pattern observed because of different particle sizes.

It doesn't always go as planned, however. They failed in some IPA analogs such as 5-NH_2-IPA, 5-SO_3H-IPA, pyrazole-3,5-dicarboxylic acid (PDA), and furan-2,5-dicarboxylic acid (FDA) to assemble into the isostructural MIP-206 family. To alleviate this issue, multivariate MIP-206 series (MTV-MIP-206 s) were also designed following the solid-solution mixed linker strategy considering varied rations of mixed linkers. The synthesized MTV-MIP-206 phases were confirmed by ^1H NMR spectra after digesting samples in KOH/D_2O solution, which clearly proves the presence of different ratios of linker units in the frameworks.

Despite the limitations, what's remarkable about the MIP-206 family is their rock-solid nature. Considering the large pores and the always fragile crystalline pore walls, it's not common to arrive stability and functionality in one go. TGA profile in air and temperature dependent PXRD data proved the preservation of long-range, ordered 2D-layer frameworks of MIP-206 s up to 450°C. In term of chemical stability, MIP-206 series show excellent hydrolytic stability at room temperature, boiling water even very harsh conditions for example concentrated HCl, base pH = 12, and aqua regia. MIP-206 series shows admirable scalability at a 10 g scale from a one-pot reaction. It is important to note that there is only a handful of reported robust mesoporous materials that show such remarkable features.[8–10]

Owing to the outstanding stability, the well-organized mesoporous MIP-206 can be used for practical use as a heterogeneous catalyst for hydrogen generation from formic acid. To do that, palladium (Pd) NPs featuring high

activity, long-term stability, good reusability, and facile process is needed. The authors optimized the loading of Pd in MIP series and realized the rattle structures with exceptional performances. Among the functionalized versions, MIP-OH came out as a compatible material in the MIP-206 family. The active catalyst is readily prepared by the reaction of MIP-OH, 3.1 wt % Pd NPs, and 2 eq. $NaBH_4$ at 60°C. The product was characterized judiciously to prove the uniform distribution of Pd.

In summary, the state-of-the-art mesoporous MIP@PdNPs that are based on MIP-206-OH and MTV-MIP-206-OH showed excellent catalytic activity toward hydrogen generation from formic acid, likely related to the pore accessibility and the presence of a specific functional group. And the icing on the cake? The heterogenous catalyst Pd(0) @MIP-206-OH worked charmingly for five consecutive runs without significant loss.[3]

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Accurate and Affordable Explicit Solvent Quantum Mechanics for Electrocatalysis Investigations

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Solvents play a crucial role in electrocatalytic reactions, yet existing simulation methods for the catalyst-solvent interface are either too slow or too inaccurate. Goddard et. al. report a quantum mechanics/ molecular mechanics method for electrocatalysis simulations which they show to be accurate and efficient.

Quantum mechanics, especially density functional theory, has been widely used in heterogeneous catalysis to explore reaction mechanisms in many gas-phase reactions. With the Langmuir adsorption model, models are simplified by considering only the catalyst surface and the adsorbate, without the explicit simulation of the gas-phase molecules. Modeling methods have been developed to evaluate activity,[1] selectivity,[2] stability,[3] and surface reconstruction.[4] Density functional theory has been reported to be sufficiently accurate to evaluate the activity of gas-phase reactions such as ammonia synthesis.[5]

For liquid phase reactions, calculation methods are less comprehensive, and this poses challenges in understanding and designing electrocatalytic materials. The solvent near the electrode, which forms part of the electrochemical double

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https://doi.org/10.1016/j.matt.2020.12.014