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A better way to produce metal-organic frameworks

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Metal-organic frameworks are porous materials that can absorb incredible amounts of substances, and researchers hope to use them to mop up pollutants or as part of fuel cells that store hydrogen gas.

Now, University of Michigan chemists have developed a simpler and more efficient method to manufacture metal-organic frameworks on a large scale that makes the MOFs as porous as possible. In fact, a single gram of the MOF produced by the chemists can soak up a football field's worth of material, if the material were laid in a single layer across the field.

MOFs are porous materials made of metal groups linked together with organic molecules—picture the connectors and rods in Tinkertoys. This construction creates structures with very high surface areas.

For example, MOFs could be used to clean pharmaceuticals from water by attracting the molecules of the pharmaceuticals and causing them to cling to the interior structures of the MOF, in a process called "adsorption." The higher the surface area of an MOF, the more material it can adsorb.

But these properties do not come easily, says Adam Matzger, the study's lead author and U-M professor of chemistry and of macromolecular science and engineering.

MOFs are often created in solvents that only boil off at very high temperatures. To make an MOF porous, chemists must "activate" the MOFs by removing that solvent. That has generally been done by bathing them in different solvents that have low boiling points for hours or days, exchanging the one solvent for the other in the MOF.

It is also difficult to remove all the replacement solvent molecules clogging the MOFs, which were placed there by the activation process. Part of the problem, Matzger says, is that the replacement solvents tended to have a high surface tension. When you pull those solvents out of the MOFs, the solvent clings to the delicate structures within MOF and can destroy them.

"When you remove something with a high surface tension from an MOF, it pulls on that pore and tends to make it collapse," he said. "By going ultra low surface tension, we're able to avoid that."

Previously, chemists had used what's called supercritical carbon dioxide, or carbon dioxide in a hybrid liquid/gas phase, held under a certain temperature and pressure.

"But it's a pain to use," Matzger said. "You need to keep it under very high pressure, and it requires specialized equipment. It's not great for producing MOFs on a larger scale."

The team also discovered that solvent swapping is extremely fast and that solvents with ultra-low surface tensions can successfully activate MOFs. Two delicate, highly porous MOFs, UMCM-9 and FJI-1, can achieve maximum surface area using solvents such as n-hexane or perfluoropentane. These solvents activate MOFs in a matter of minutes, allowing them to transition from objects of curiosity in the laboratory to the next generation of industrially important adsorbents.

"We think it's a very easy alternative," Matzger said. "You can use solvents off the shelf instead of specialized supercritical carbon dioxide."

More information: Jialiu Ma et al. Rapid Guest Exchange and Ultra-low Surface Tension Solvents Optimize Metal-organic Framework Activation, *Angewandte Chemie International Edition* (2017). DOI: 10.1002/anie.201709187

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