

THE HOLE STORY

Swiss-cheese-like materials called metal–organic frameworks have long promised to improve gas storage, separation and catalysis. Now they are coming of age.

BY MARK PELOW

Sprawled across a vast site on the river Rhine in Germany is a small city built from glittering steel: the headquarters of chemical giant BASF. Boasting a daytime population of about 50,000 people, it is criss-crossed by a grid of streets bearing names that commemorate the company's stock in trade: Methanolstrasse, Ammoniakstrasse, Gasstrasse.

Over the past two years, a small fleet of delivery vans and cars has clocked up thousands of kilometres on these streets while carrying a big secret: fuel tanks packed with an unusual crystalline material that is riddled with pores roughly a nanometre wide. Inside these pores sit methane molecules arrayed in neat stacks, ready to fuel the vans' combustion engines.

The crystals are metal–organic frameworks (MOFs), molecular scaffolds made up of metal-containing nodes linked by carbon-based struts

(see 'An open box'). The resulting pores are ideal for trapping guest molecules and, in some cases, forcing them to participate in chemical reactions. And they can be tailored with exquisite precision: researchers have created more than 20,000 types of MOF, with potential applications that range from stripping carbon dioxide from power-plant exhausts to separating intractable industrial mixtures, catalysing chemical reactions and revealing molecular structures. "MOFs are the fastest growing class of materials in chemistry today," says Omar Yaghi, a chemist at the University of California, Berkeley, and one of the pioneers of the field.

MOFs were long thought to be too frail for use in the real world, often collapsing as soon as the guest molecules were removed. Many researchers were sceptical that the products could ever compete against the tough inorganic materials called zeolites, whose pores are exploited in a wide variety of industrial processes, including filtration and catalysis.

But after more than a decade of intensive research in labs around the world, MOFs are poised to make their debut in commercial applications. Although unwilling to reveal the identity of the MOF in question, BASF has said that it is ready to market a methane-storage system this year that can cram in much more fuel than a conventional pressure vessel.

MOF researchers say that this milestone would be a shot in the arm for their work, and potentially help to stimulate commercial interest in the many other applications that are close behind, often from other producers.

STORAGE WARS

Much of the ferment in MOFs dates back to 1999 and the debut of two unusually robust varieties: HKUST-1, developed at the Hong Kong University of Science and Technology¹; and MOF-5, developed by Yaghi². The latter has an internal surface area of at least 2,300 square metres per gram — enough to cover more than eight tennis courts. "That was the turning point, because it broke all surface-area records," says Yaghi. "Years later, BASF told me that they thought it was a misprint."

More internal surface area means more places to stack guest molecules, and Ulrich Müller, who leads BASF's research on porous materials, was quick to see an opportunity. "We started working on MOFs directly after Yaghi's paper," he says, and the pair quickly forged a collaboration that continues to this day.

The key to making stable MOFs is to use clusters of metal atoms as the nodes, rather than individual ions. The geometry of the clusters determines the overall architecture of the crystal, which can be held together by a cornucopia of organic linkers. The growing set of interchangeable Tinkertoy components makes MOFs much more adaptable than zeolites and enables chemists to design products with pores that have just the right size and chemical properties for specific applications. Today, there are MOFs that can withstand temperatures of 500 °C, or easily endure a week in boiling methanol; others have internal surface areas that are triple that of MOF-5, or pores large enough to accommodate chunky proteins³.

BASF currently dominates the nascent MOF market. It has targeted methane storage because shale gas is cheap and increasingly available, so could be used to power automobiles that incur lower running costs and generate less CO₂ than conventional vehicles. However, at present, the gas needs to be stored in bulky and expensive high-pressure tanks, which is a major disincentive. MOFs could overcome that by storing more methane at lower pressures.

To make that application work, the size and chemical properties of the MOF's pores must be just right, because they determine how the methane molecules stack up inside. "If you just have methane floating inside the pore, you might as well use an empty canister," says Yaghi.

To tie down the methane, researchers use MOFs with pores that boast exposed metal ions. The ions distort methane's electron cloud, polarizing it so that the gas molecules stick to the metal. But if the pores bind to methane too weakly, the gas will leak out; too strongly, and the vessel will be hard to empty. The

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best MOF crystals occupy a Goldilocks zone that gives them at least twice the capacity of an empty vessel at moderate pressure, yet still allows them to release almost all their methane as the pressure drops. "Methane storage for automobiles is largely a solved problem," says Yaghi.

Commercial success is far from guaranteed, however. Since the price of crude oil began to plummet last year, the economic incentive of gas has disappeared. "This gap is currently almost non-existent," says Müller. "Everything is in a little bit of turmoil because of that."

Market-watchers predict that the price of oil will rebound sooner or later. But in the meantime, Jeffrey Long at the University of California, Berkeley, says that there is ample scope to improve MOF methane-storage systems. In collaboration with Yaghi, BASF and the Ford Motor Company, he is aiming to reduce the pressure needed to fill a tank. "If you go down to 35 bar, people can potentially fill their cars at home," he says. Long and his colleagues say that they have created a MOF that stores more methane than the best current compounds at low pressure and are preparing to publish their results. "We can beat it by a reasonable margin," Long says.

MOFs could make an even bigger impact on transportation by storing hydrogen for fuel-cell vehicles. Compressing chilled gas into high-pressure tanks is complex and expensive. But replacing those tanks with MOFs that can store useful amounts of hydrogen is a tough challenge. "There's no absorbent out there that has a high enough capacity to be used commercially," says Long.

Long's team has developed⁴ a record-breaking nickel-based MOF that binds to hydrogen strongly enough to carry 12.5 grams of the gas per litre of storage tank at room temperature and 100 bar. That is, however, well short of the US Department of Energy's hydrogen-storage target for 2020, which calls for a corresponding figure of 40 grams per litre. Using MOFs with metal ions in their pores that can each bind to several hydrogen molecules could bring researchers closer to that goal.

In the meantime, others are looking to commercialize MOFs for niche gas-storage applications. Omar Farha at Northwestern University in Evanston, Illinois, co-founded the spin-out company NuMat Technologies in Skokie, Illinois, in 2012 to develop MOFs that can safely store some of the toxic gases used in the semiconductor industry, including boron trifluoride, phosphine and arsine. "We're doing something different from everybody else," he says. "It's a smaller market that we can capitalize on very quickly."

Farha reckons that the company's first product will launch in the next two years, helped by a recent boom in the use of computer modelling to predict the properties of MOFs. In 2012, Farha and his colleagues showed that they could reliably screen almost 140,000 hypothetical MOFs for their methane-storing ability⁵, and now they are saving time and money by synthesizing only those MOFs that show promise in similar computational tests.

TRIAL SEPARATION

Researchers are also hoping that MOFs can pluck specific molecules out of the air — literally. "Gas separation, in particular, is where these materials could have a competitive advantage," says Long.

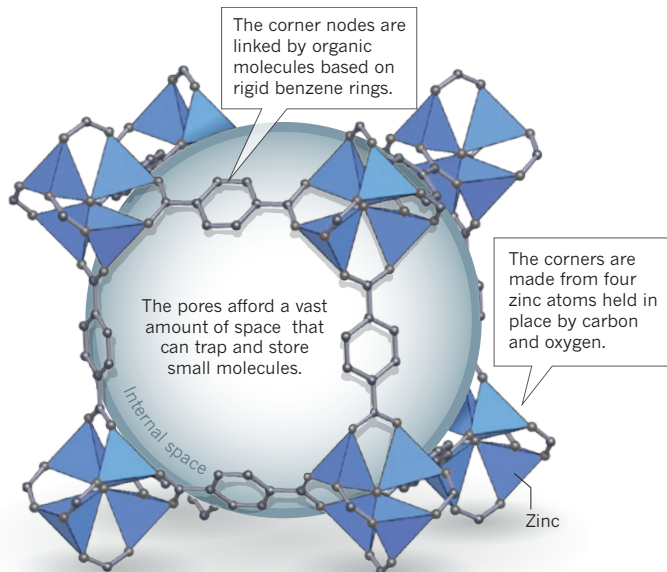
They could be particularly attractive for industrial cracking plants, which heat crude oil to break down large molecules into light hydrocarbons. These gases can be extremely difficult to separate. Propene and propane differ by just two hydrogen atoms, for example, and their boiling points are only around 5 °C apart. At the moment, refiners isolate them by cooling the mixture until it liquefies, then warming it slowly so that first one gas and then the other boils off. But these temperature swings make it one of the most energy-intensive processes in the chemical industry.

Long's group has shown that a crystal known as Fe-MOF-74 makes the job easier and potentially much less costly. The crystal's exposed metal cations can latch onto the electrons of a passing propene molecule, slowing down its passage. At a balmy 45 °C, propane emerges first; warming the MOF then frees a 99% pure stream of propene⁶. Another crystal, Fe₂(BDP)₃, can efficiently separate isomers of hexane⁷, which comes in

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AN OPEN BOX

One of the first metal–organic frameworks to be rugged enough for practical use was a crystal known as MOF-5. Its building blocks are cubes formed by linking together eight metallic nodes with carbon-based struts.



linear and variously branched forms. The linear molecules get stuck in the corners of the MOF's triangular channels, an architecture that Long says would be impossible to achieve with zeolites.

Perhaps the ultimate test of MOF-based separation would be to capture some of the 13.7 gigatonnes of CO₂ produced by fossil-fuel power plants each year. Conventional carbon-capture systems rely on solvents that react with the CO₂ in a power station's 40 °C exhaust stream. Removing and heating the solvent to 120 °C or more frees the gas for collection and storage. But swinging the temperature back and forth eats up 20–30% of the plant's power, and requires expensive infrastructure.

Last month, Long's team showed⁸ that magnesium- and manganese-based MOFs could absorb and release more than 10% of their weight in CO₂ from flue gas with a temperature swing of just 50 °C. Their pores are lined with amine molecules that are similar to the solvents already used for carbon capture, and react with CO₂ to produce chains of tightly packed ammonium carbamate molecules.

A similar, as yet unpublished MOF can release its carbon cargo below 100 °C, and Long hopes to test it at the US National Carbon Capture Center in Wilsonville, Alabama. It has a higher working capacity and lower temperature swing than solvent systems, so Long expects to be able to reduce the size of the capture unit and cut infrastructure costs; he has already co-founded a start-up company, Mosaic Materials in Berkeley, to produce the MOFs.

CRYSTAL SPONGES

Industrial-scale development of any new material is slow work. But applications can blossom remarkably quickly if only small quantities are required. Just two years ago, Makoto Fujita at the University of Tokyo developed a MOF that can help to determine the structure of pharmaceuticals and other organic molecules. Now he is deluged with commercial interest.

Many organic molecules steadfastly refuse to form crystals, which normally rules out using the conventional technique of X-ray crystallography to determine the precise spatial arrangement of their atoms. But in 2013, Fujita's team showed that a zinc-based MOF could soak up molecules of miyakosyne A, a natural marine product, and hold them steady in its pores so that X-rays can reveal their structure⁹.

"I thought, 'Wow! This is a way to revolutionize the way organic chemistry can progress,'" says Phil Baran, an organic chemist at the Scripps Research Institute in La Jolla, California.

Others, however, were less impressed. Crystallographers found the MOF's performance hard to reproduce, and then Fujita's team found an error¹⁰ in its structure of miyakosyne A, making others wary of the technique. Since then, however, Fujita and others have produced detailed instructions¹¹ that are winning over sceptics. The technique cannot handle all molecules, but Fujita thinks that 20–30% of the organic compounds they test can have their X-ray crystal structure determined in this way, using as little as 5 nanograms of the guest molecule.

Last year, the Japan Science and Technology Agency awarded Fujita US\$15 million over five years to help him to commercialize the method, and some pharmaceutical companies are now using the technique to assist drug development. And a Japanese reagent company plans to make Fujita's crystal sponge — and the successors being developed in his lab — available off-the-shelf within the next three years.

GO-FASTER MOFS

Catalysis has long been touted as one of the most promising applications for MOFs. Their tunable pores can hold reagents in place, cleave specific bonds and then forge new ones, just like the active site of an enzyme.

But until a few years ago, progress on such catalysts was very slow, says chemist Joseph Hupp at Northwestern University, not least because very few MOFs were chemically stable enough to put through multiple rounds of reactions¹². As a result, says Hupp, "there is not yet an example of a reaction for which MOFs are so superior that a typical organic chemist would choose a MOF-based catalyst over an existing catalyst".

Now, however, researchers are making promising catalysts by taking stable MOFs and tweaking the chemical groups around their pores³. They have also gone one stage further, gradually swapping out entire linkers or metal nodes to transform the MOF's chemical and physical properties without collapsing the whole structure¹³. These advances have allowed chemists to design and make a much wider variety of rock-hard but chemically-active MOFs. "There's a lot of MOFs now that we just couldn't make five years ago," says Hupp.

Indeed, one of the growing challenges for the field is the bewilderingly large number of MOFs. "We have too many," says Yaghi. Hupp agrees. Researchers need to dial back on synthesizing MOFs whose properties are never fully explored, he says, and instead focus on refining those that have proven stability or activity.

Another challenge is that MOFs have to compete with incumbent technologies such as zeolites. This puts a premium on getting the cost down by making MOFs from abundant metals and cheap organic linkers that can be manufactured in safe and inexpensive processes. BASF, for example, is making MOFs at the tonne-scale in water, rather than in other solvents.

Yet MOFs can compete through their originality. Yaghi is developing MOFs that contain several types of pore within the same crystal, so that molecules would undergo a predefined sequence of reactions as they pass from one region to the next¹⁴. These MOFs could behave like microscopic versions of a chemical plant, allowing scientists to synthesize molecules piece by piece in a continuous process.

"That's our dream," says Yaghi, "and it's only possible in MOFs." ■

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