

Magic MOFs

Metal organic frameworks are molecular mops that have the potential to solve some of the world's most pressing environmental problems. Hayley Birch finds out more

Targets for reducing greenhouse emissions seem worryingly over optimistic. Even the relatively conservative target of the G8 nations, to halve emissions by 2050, will require cuts of hundreds of millions of tonnes of carbon dioxide every year. And as we are continually reminded, the consequences if we do nothing will be dire.

As emissions statistics map a skywards trend, the attitude of those who claim 'technology' will yield a solution may appear frustrating. Two of the most promising solutions are to capture and store these carbon emissions, and to develop clean fuels based on hydrogen. But before either can make any real impression on global emissions, one major practical problem has to be overcome: gas storage.

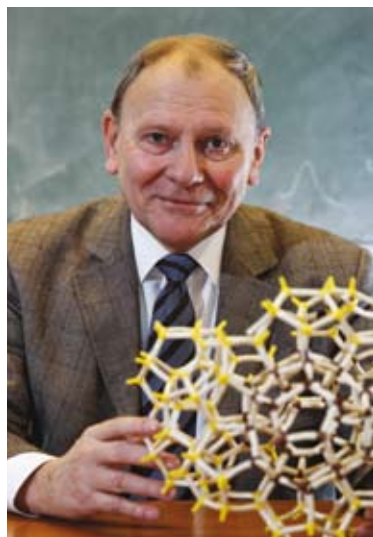
The dream would be to have a material that could be used to safely store huge quantities of hydrogen or carbon dioxide. And that's where MOFs come in. Over the last decade, crystalline structures known as metal organic frameworks have attracted the interests of scientists for their sponge-like ability to mop up extraordinary volumes of gas. This ability, due to their large surface area to weight ratio (see box p49), outstrips that of many commercially available porous materials, including activated carbon and microporous minerals such as zeolites.

Of course, the accommodating nature of MOFs makes them perfect

for a variety of other applications besides storage. Researchers are also developing these materials to perform gas separations, as sensors, and even as delivery vehicles for slow-release medicines. Perhaps most intriguing of all though, is the eventual goal of combining storage with catalysis, so that one day it could be possible to use MOFs not only to capture carbon dioxide but also to transform it into useful fuels.

Storage solution

MOFs are essentially solids in which metal atoms are joined together by organic linkers. Pore size and performance depend on the combination of metal and linker, as



In short

- MOFs are highly porous crystalline solids that can soak up prodigious amounts of gas
- MOFs could be developed to store hydrogen fuel, or to capture carbon dioxide
- Researchers are already looking to incorporate further functionality into the framework, moving from gas storage to sensors
- By incorporating catalytic groups into the organic linkers, trapped CO₂ could one day directly be converted back into a useful fuel or feedstock

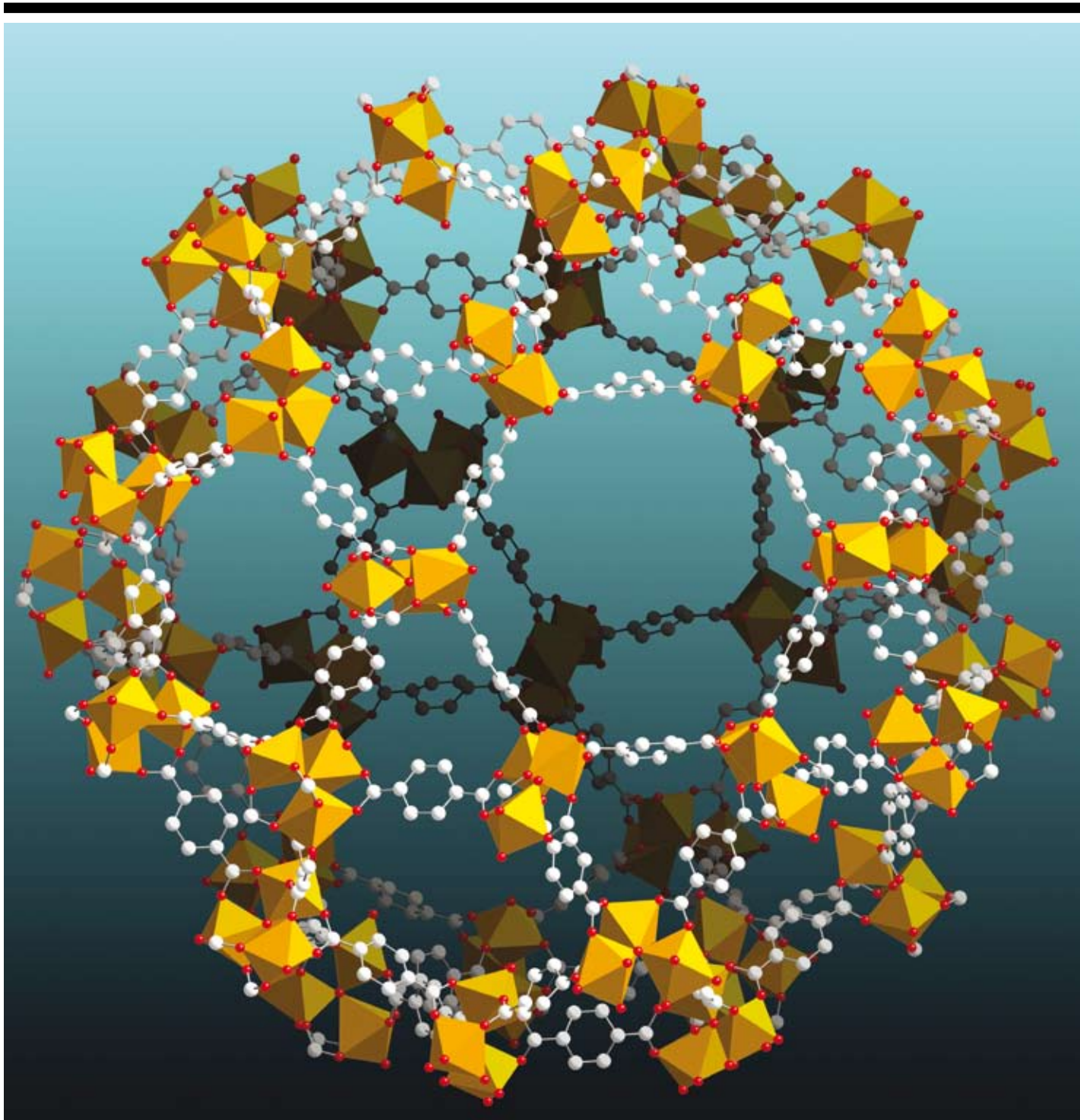
Gérard Férey's MOFs hold record-breaking quantities of carbon dioxide

well as the structure in which they are connected. Clearly, this leaves a lot of room for manoeuvre, which is why identifying the combinations with the most interesting properties can be quite a challenge.

It is possible to design useful MOF structures by computer simulation, but only after painstaking work in the lab to discover how the component parts behave under reaction conditions. In 2005, this technique delivered a hit for a group led by Gérard Férey at France's national research agency CNRS. They measured the surface area of their chromium-based MOF, MIL-101, at 5900m² per single gram¹ – getting on for the size of a football pitch. But even more impressive is its capacity for carbon dioxide. In 2008, Férey's team announced that MIL-101's huge pores have the capacity to hold around 400m³ of carbon dioxide per cubic metre of crystal at room temperature;² MIL-101, it seems, is the molecular equivalent of the Tardis. 'This solid is really the best solid for trapping CO₂ and it's an unbelievable performance,' says Férey. 'It's a magic solid.'

Férey says he is already in discussions with several companies keen to develop MIL-101 for commercial use. 'We can imagine applications for cars, trapping CO₂ from the gas exhaust, or putting this solid in chimneys to store CO₂,' he says.

One company interested in



GERARD FÉREY / DAVID PALMER

developing MIL-101 is BASF, which already markets MIL-100 – a MOF with slightly smaller cavities – for hydrogen storage. But it is hydrogen that poses the greater challenge, says Férey. Many MOFs with unprecedented hydrogen storage capacities are practically unusable because they only work at extremely low temperatures. MIL-101, for example, has one of the highest hydrogen storage capacities per volume of solid, but at an icy -196°C (77K). Férey thinks MOFs more

generally may ultimately be limited in their use as hydrogen containers.

Jeffrey Long, a MOFs expert at the University of California, Berkeley, US, explains that the problem arises from the nature of the interaction between hydrogen and the types of MOFs studied so far.³ ‘They mainly have just a weak Van der Waals type of interaction and that interaction is extremely weak for hydrogen because it has just two electrons. So they work very well at low temperatures but if you try and load them with hydrogen

MIL-101 hides a football pitch sized surface area inside every gram of the crystal

at higher temperatures, the thermal energy overwhelms the interaction and you see very little capacity.’

Nevertheless, Long’s outlook is hopeful. His team are trying to embed exposed metal centres into their structures. Incorporating a $2+$ or $3+$ charge at the material’s surface, he says, should induce a dipole in a hydrogen molecule, resulting in a stronger interaction. The choice of appropriate metals, however, is limited by their weight, as to find practical use in hydrogen

fuel tanks the material would need to be relatively light. Long thinks magnesium or aluminium, bridged by azolate linkers, might make the perfect combination.

The team's eventual goal is to design MOFs which would operate at near room temperature and, crucially, closer to atmospheric pressure, in order to improve the safety of hydrogen fuelled cars. 'Right now, most hydrogen cars run on high pressure hydrogen gas – sometimes 500 bar – to get a decent range on how far they can go,' he says. 'The idea is that with this adsorbant in the tank you could pressurise to maybe 100 bar. That's a safer pressure and so you could get away with cheaper cylinder materials.'

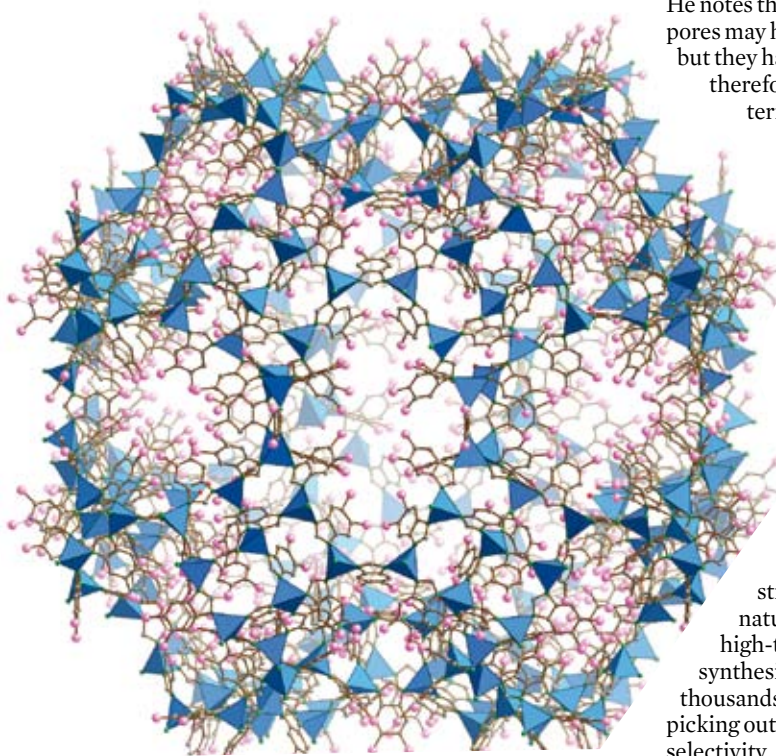
According to Long, there is increasing interest from industry in developing MOFs for use in hydrogen cars. Low pressure storage materials would reduce the risk of in-car explosions, as well as the almost prohibitively high costs associated with transporting hydrogen fuel.

But one of the main criticisms levelled at hydrogen technology is that the hydrogen itself is often produced by burning fossil fuels. Perhaps hydrogen producers could use some MIL-101 in their chimney stacks, says Férey.

More than a mopping job

Mopping up and storing a gas requires more than just a molecular sponge – a really useful material would have high selectivity for the gas it was intended to store. Here again, MOFs come up trumps. Late in 2008, US and UK scientists reported the synthesis of flexible frameworks which could swell or 'breathe' under pressure to selectively accommodate carbon dioxide.⁴ The researchers, led by Jerry Atwood at the University of Missouri-Columbia, think their material – made from zinc atoms connected by organic linkers – is able to discriminate between gases based on their shape and size. Despite small pores, it retains carbon dioxide, whilst letting nitrogen and hydrogen slide right through.

'The way that selectivity arises is not clearly known for any of these systems just yet,' says Atwood. 'But it's



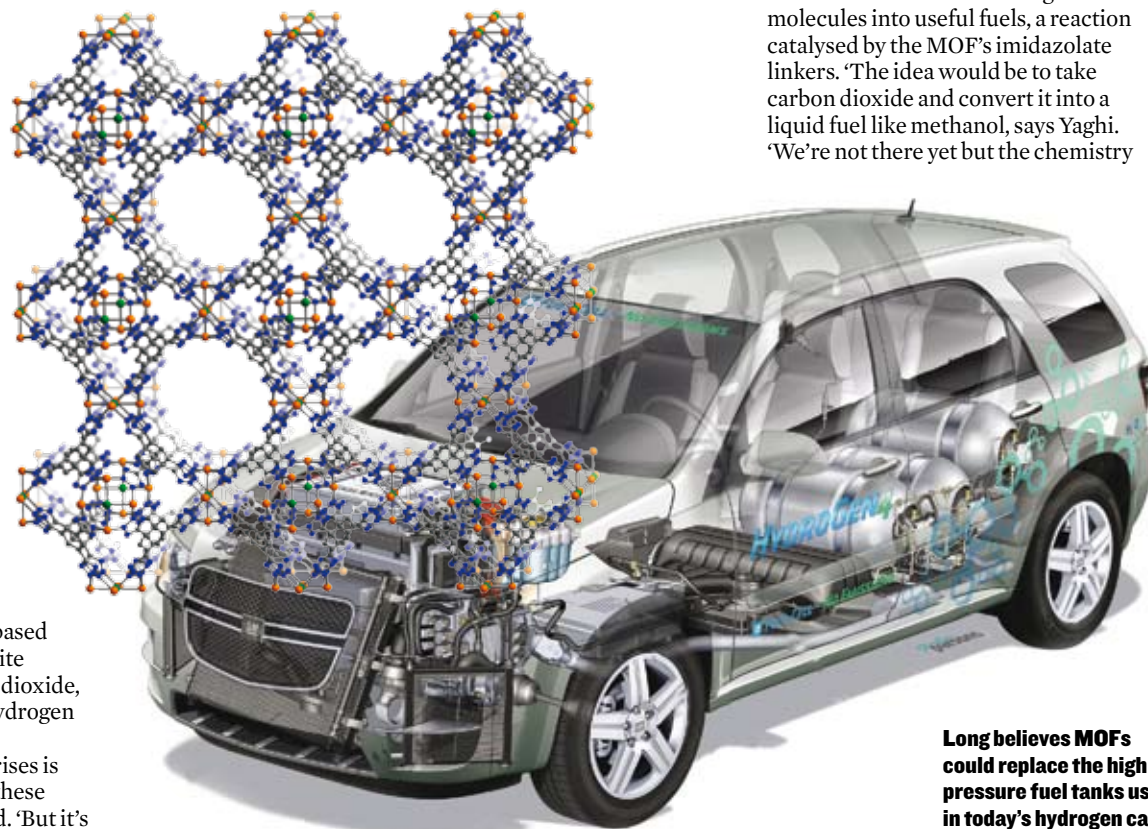
almost a sort of folklore among people in the carbon industry that in order for a molecule to be retained it needs to fit into a pore, a layer or a cavity that is of the order of two or three times the diameter of the molecule.'

ZIFs feature imidazolate linkers that could be used to add further functionality

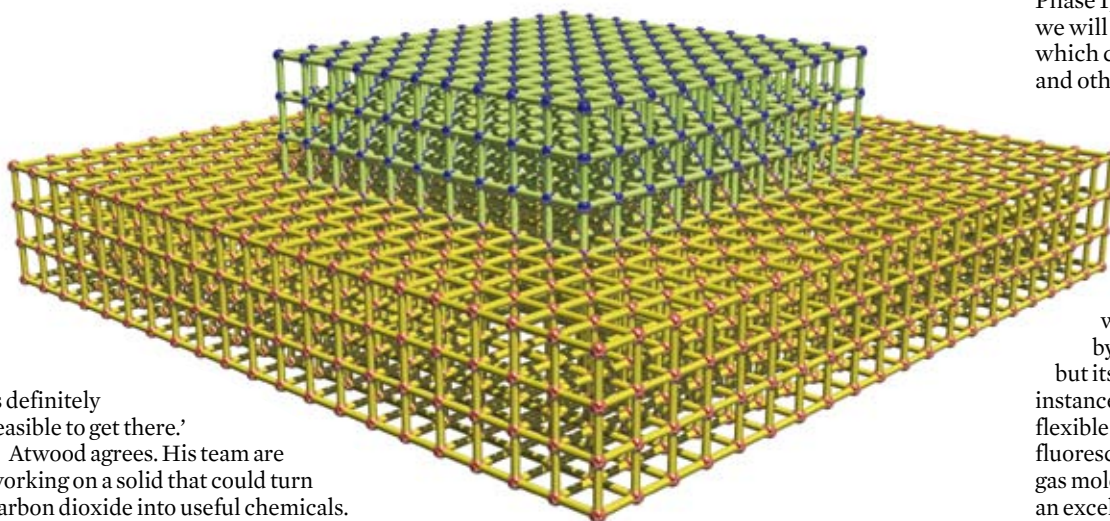
He notes that materials with bigger pores may have larger surface areas, but they have limited selectivity and therefore may remain limited in terms of their functionality.

MOF scientists at the University of California, Los Angeles (UCLA) have unveiled a whole new class of MOFs, some of which they recently designed with 'revolving doors' – functional groups that keep out unwanted guests – on their linkers (see *Chemistry World*, June 2008, p23).⁵ They call their materials zeolitic imidazolate frameworks (ZIFs), because of their structural similarity to natural zeolites. Using a high-throughput approach to synthesis, the researchers tested thousands of structures before picking out those with the highest selectivity.

ZIFs have large pores and are well suited to capturing carbon dioxide, says Omar Yaghi, who heads the team. But Yaghi's vision extends beyond simply capturing and storing the gas. He says the best long term solution would be to create a material that could also transform its guest molecules into useful fuels, a reaction catalysed by the MOF's imidazolate linkers. 'The idea would be to take carbon dioxide and convert it into a liquid fuel like methanol, says Yaghi. 'We're not there yet but the chemistry



Long believes MOFs could replace the high pressure fuel tanks used in today's hydrogen cars



is definitely feasible to get there.'

Atwood agrees. His team are working on a solid that could turn carbon dioxide into useful chemicals. 'If we could adsorb CO₂, but then catalytically convert the carbon into carbonic acid or a carbonate salt, then we wouldn't have a gas that we had to inject into the centre of the Earth to keep it from contributing to global warming,' he says. 'Rather, we would be capturing the CO₂ and converting it into a condensed phase – a solid or a liquid, which could then be used for other chemical processes.'

Compared to the gas storage applications of MOFs, however, catalytic applications are just beginning to be explored. This is perhaps partly because incorporating components that catalyse chemical reactions adds a further layer of complexity to screening for interesting MOFs. Finding a material that has a high surface area is one thing, but designing a material which also has high selectivity for its guest molecules and incorporates specific catalytic components is quite another.

But that's the exciting part, says Yaghi, who is optimistic about the future for his ZIFs. 'Remember, these are only three years old, so there's a natural progression of things, but already we can make more structures

than zeolites,' he says. 'So now it's about functionalising them and doing chemistry in the pores.'

Eventually, MOFs could mimic nature by functioning as artificial enzymes. Their high density of pores means they have the potential to house not just one, but vast numbers of catalytic sites. Pore dimensions can be finely tuned to influence reactivity – a level of control not accessible to those working with zeolites or activated carbon. Linkers can even incorporate chiral components which could lead to catalysts optimised to generate one enantiomeric (mirror image) version of a product.

Wonder materials

The infinite diversity of the frameworks has led researchers to speculate about all manner of interesting applications.

According to Susumu Kitagawa, who works on MOFs at Kyoto University in Japan, MOF scientists are on the brink of creating compounds with unique and unprecedented properties. 'We are in a kind of period that we call

Kitagawa's 'Phase I' MOF is just the beginning

Phase I,' he says. 'In the next phase we will synthesise compounds which can not be obtained for zeolite and other systems.'

Kitagawa says 'Phase I' has been about identifying the single properties of MOFs – storage, separation and so forth. But in the future, he hopes to develop MOFs with integrated properties, which could be enhanced by utilising not just the MOF, but its guest molecule as well. For instance, he explains, a MOF with flexible electrical conductivity or fluorescence depending on how much gas molecule was loaded could make an excellent sensor.

He is also entering into a collaboration with researchers at Ruhr University Bochum in Germany to create 'SURMOFs' – ultra-thin films of MOFs that are applied to surfaces. The idea is to develop them as intelligent membranes and sensors for electronic devices.

Collaboration, says Kitagawa, is the only route to integrated properties – by encouraging researchers from many different fields to work together. 'In my lectures I invite many people to come into this field – from biochemistry, biological sciences, physics, everywhere.'

In a field where so much stands to be gained, particularly when the environmental applications of MOFs are considered, it is almost overwhelming to imagine the breadth of research that will follow in years to come. 'The bad news is that we have to solve the problem, whether it's gas storage, separation, catalysis, or the embodiment of some of these three things into sensors,' says Atwood. 'The good news is that I don't have to solve it and you don't have to solve it, but somebody has to.'

Hayley Birch is a freelance science journalist based in Bristol, UK

To read more on MOFs look out for the upcoming themed issue in Chemical Society Reviews, guest-edited by Jeff Long and Omar Yaghi

References:

- 1 G Férey *et al.*, *Science*, 2005, **309**, 2040 (DOI: 10.1126/science.1116275)
- 2 S. Bourrelly *et al.*, *Langmuir*, 2008, **24**, 7245 (DOI: 10.1021/la800227x)
- 3 M Dincă and J R Long, *Angew. Chem. Int. Ed.*, 2008, **47**, 6766 (DOI: 10.1002/anie.200801163)
- 4 P K Thallapally *et al.*, *J. Am. Chem. Soc.*, 2008, DOI: 10.1021/ja806391k
- 5 B Wang *et al.*, *Nature*, 2008, **453**, 207 (DOI: 10.1038/nature06900)

'The ideal would be to take carbon dioxide and convert it into a liquid fuel like methanol'

Cleaning out the pores

Massive gains in surface area can be achieved by a process called 'supercritical drying', which opens up access to MOFs' cavernous pores. Having used a similar method to create high-area electrodes, Joseph Hupp's team at Northwestern University and Argonne National Laboratory, US, wondered if supercritical carbon dioxide, which behaves in some ways like a gas and others like a liquid, could increase the surface area of their zinc-based MOFs. 'Sort of on

a lark we tried this,' says Hupp. 'We had the apparatus at hand and CO₂ is cheap.' Following their intuition paid off. Because supercritical CO₂ has no surface tension, explains Hupp, the MOF particles aren't pulled together when the fluid is removed, leaving the channels unblocked. The team have shown 12-fold increases in surface area using supercritical drying.

Reference:

- AP Nelson *et al.*, *J. Am. Chem. Soc.*, 2008, DOI: 10.1021/ja808853q