New construction kit for chemists

TU Delft is heading a European research programme on CO_2 capture, with a budget of €10 million. This could result in the first large-scale application of a new class of porous materials.

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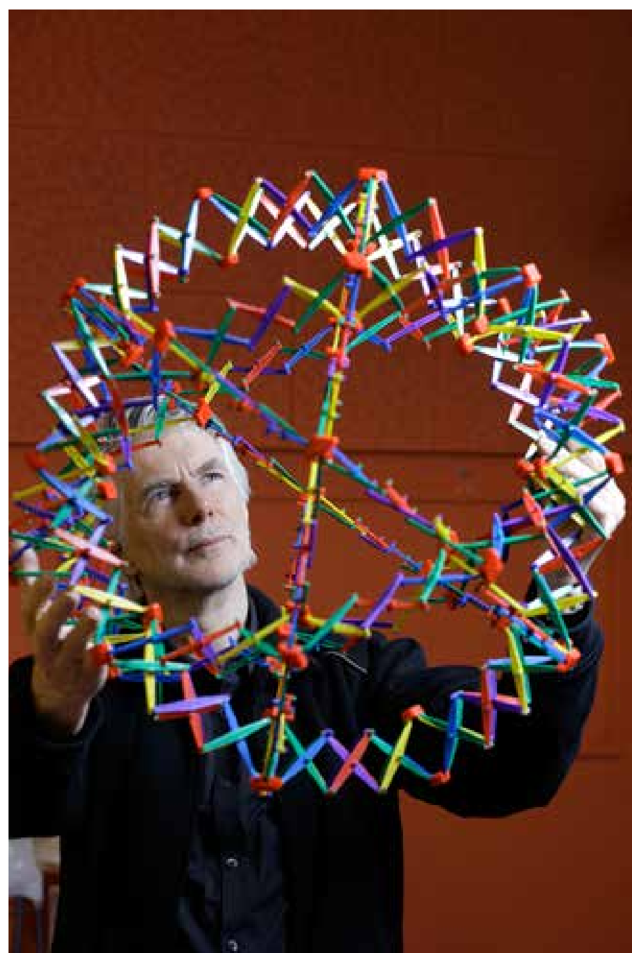

The prestigious M4CO_2 research project was launched in early February in the ChemE catalysis laboratory of Prof. Freek Kapteijn and Prof. Jorge Gascon (Applied Sciences). Sixteen European partners are involved in the project, which is part of the European Seventh Framework Programme.
Within four years, the project is expected to result in the development of membranes that allow the selective permeation of CO_2. This will make it possible to remove CO_2 from flue gasses, as desired by the European Union (EU).
The process would eventually be considerably less expensive than the current method, which involves fluids (amines) that bind with CO_2 at low temperatures and release it at high temperatures. Raising and lowering the temperature costs a lot of energy, and therefore money. According to a recent report from the Massachusetts Institute of Technology (MIT), the cost of CO_2 capture ranges from €30 to €90 per ton, depending upon the type of power station. The EU is aiming for a continuous process, with a target price of €15 per ton.
The price of the CO_2 capture will determine whether the technology will be used or whether the greenhouse gasses will be released into the atmosphere. According to recent estimates, the capture and storage of CO_2 costs at least €45 per ton. Emission rights on the European emissions market (EEX) are at less than €6 per ton of CO_2. What would you do?
'Reductions in the emission of CO_2 from major sources, such as coal-fired power stations and other energy-intensive industries, could help in the fight against climate change', argues Dechema, one of the research partners, in a press release. For this to happen, however, sequestration would have to be so inexpensive that industries would apply it. This is the most important idea underlying the M4CO_2 research programme 'mixed matrix membranes based on metal-organic frameworks (MOFs) and polymers for continuous CO_2 separation'.
'To date, people pinned their hopes on membranes made of polymer or zeolites', explains Dr Jorge Gascon, an associate professor in Kapteijn's catalysis department. Each of these membranes, however, has its own deficiencies. Polymer membranes are not permeable enough for the large amount of gas that must pass through them. Zeolite membranes are too brittle. 'The new approach proceeds from a polymer with built-in CO_2 filters', Gascon explains. 'This combines the simple production of a polymer with the selectivity of porous material. MOFs are very good at this.'

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CONSTRUCTION KIT

MOFs – short for 'metal oxide frameworks' – are the new construction kit for chemists. Their most remarkable property is that they are extremely hollow. 'One gram of material has an internal surface the size of a football field', explains Gascon. Although it is difficult for laypeople to imagine, chemists were quite excited by this in the 1990s. 'To a chemist, space inside a molecule is the same thing as a large house is to a designer: a world of possibilities.'
Prof. Freek Kapteijn shares this enthusiasm: 'MOFs can be used as a gate that allows or blocks the permeation of specific molecules, as a catalyst (which causes molecules to react with each other – ed.) or as storage for hydrogen or other substances. They can be activated thermally, electrically or with light. It's really a construction kit with countless possibilities.'
To date, tens of thousands of MOF variants have been developed. One property that they all share, however, is the combination of a metal atom with organic molecules as branches. As Gascon describes it, 'You can choose whichever metal you like, along with a random organic "linker" (in many cases, organic acids – ed.), and combine them however you like. The possibilities are virtually unlimited.'
Gascon explains that the preparation of MOFs is a lot like cooking in a pressure cooker. He shows a sturdy steel cylinder used for this purpose. The cylinder is filled with a mixture of a salt (for the metal cores) and a multiple carbon acid dissolved in water or an organic solvent. The proper proportions determine the end product – a layer of white, yellow or light-green powder, depending upon the metal used.
As in the kitchen, mastery is revealed in the details. 'By changing the conditions, it is possible to steer the process in a certain direction', says Gascon. The temperature, the salt used, the type of acid that is added, the proportions of the mixture and the choice of whether to use a solvent all affect the ultimate result.

APPLICATIONS

One of the first applications is in the form of a catalyst, facilitating chemical processes.

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Smartly dimensioned molecules in the MOFs could serve as antennae for visible light. Kapteijn explains: 'These antennae collect energy from the photons and bring the metal core to a higher energy level, such that it can start a chemical reaction.'
One application that could save a great deal of energy is the separation of ethene and ethane. This separation of gasses is highly important for the chemical industry, which must invest large amounts of energy to cool the gas mixture to a point at which the gasses condense. One solution could be MOFs that bind ethane more strongly than they bind ethene.
Other promising uses for MOFs include the storage of hydrogen gas. According to Gascon, a gas cylinder filled with MOFs can contain nearly the same amount of hydrogen gas as a cylinder containing liquid hydrogen. The difference is that the cylinder containing MOFs would not have to be cooled.
The European M4CO_2 programme has made possible the first large-scale application of MOFs in the area of CO_2 capture. They could also be applied for the selective permeation of hydrogen gas, which is covered by the project as well. 'The greatest challenge will be to make membranes that will allow the permeation of enormous streams of gas', observes Gascon. 'This means that the resistance will have to be very low and that we will have to work with ultra-thin separation layers. This will require an exceptionally good match between the polymer (for the membrane) and the MOFs (as pores – ed.). We are therefore developing the chemistry for both the MOFs and the polymer.'
The filter material will be processed into long, hollow straws that are packed together in a bundle to form the gas filter. When flue gasses are blown through the filter, only CO_2 should be able to permeate the membrane.
At the end of the project, in four years' time, the consortium hopes to deliver two modules: one for CO_2 capture and one for hydrogen separation. These will be tested for at least two months under realistic conditions by one of the industrial partners. <<

Why this is important

The emission of CO_2 is continuing to increase throughout the world. The use of membranes to remove CO_2 from flue gasses is less expensive than the current method, using liquids. This is an important point, given that the price of CO_2 capture will determine whether the technology will be used or whether the greenhouse gasses will be released into the atmosphere.