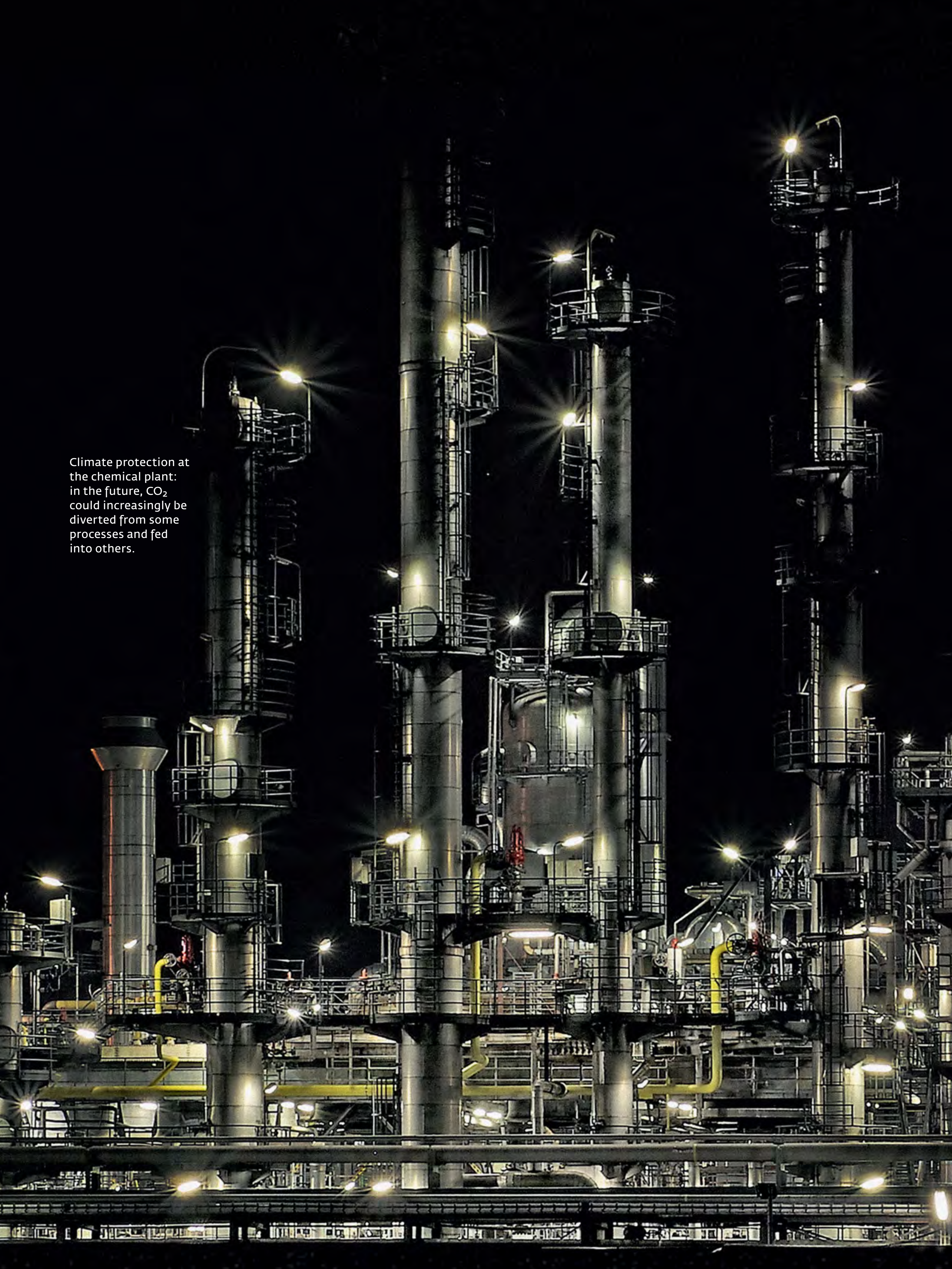


Climate protection at the chemical plant: in the future, $CO_2$ could increasingly be diverted from some processes and fed into others.

# **A greenhouse gas** to fuel the chemical industry

Carbon dioxide, of all substances, could help the chemical industry reduce its climate footprint. Using energy from renewable sources, it could be incorporated into the building blocks of plastics and other products – if suitable catalysts and production processes can be found. That is the task of researchers led by **Walter Leitner** at the **Max Planck Institute for Chemical Energy Conversion** in Muelheim an der Ruhr.

TEXT **PETER HERGERSBERG**

A conversation with Walter Leitner can change the way you see the world. Afterwards, when you look around, you may well see one thing in particular: carbon. That's hardly surprising – as an element of life, carbon forms the chemical backbone of every living organism and is an integral component of organic matter that nature provides, including wood, starch, and cotton.

But carbon is also omnipresent in plastics, in the dyes for our clothes, in medications, and in fuels. Even if we consider these products to be artificial, they wouldn't exist without nature's input. "Through photosynthesis, plants that were alive millions of years ago absorbed the carbon we use today in the form of coal, oil, and natural gas – both as an energy vector and as a raw material for chemical production," says Walter Leitner, Director at the Max Planck Institute for Chemical Energy Conversion in Muelheim an der Ruhr and Professor of Technical Chemistry at RWTH Aachen University.

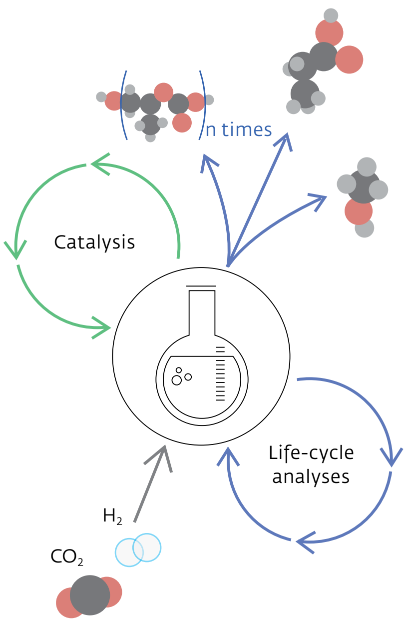
However, if we humans want to preserve the Earth in its current form, we can no longer rely on this fossil-based form of economic activity. Sooner or later, all carbon-containing raw materials end up as $CO_2$, most of which is released into the atmosphere, where it causes an imbalance in the natural carbon cycle. Many national economies are taking action with the goal to reduce their carbon footprint. In Germany and around the world, an increasing proportion of our electricity is now derived from renewable sources – especially wind and solar power. In this way, we could gradually eliminate our energy supply's reliance on fossil resources – and, indeed, on carbon itself.

"But we will always need carbon in the chemical value chain," says the chemist. If nothing else, therefore, he wants to contribute to ending the reliance on fossil sources of carbon in chemical production and has set his sights on $CO_2$ of all substances – the waste product that does the greatest harm to the reputation of fossil raw materials. Above all, Walter Leitner and his team want to use $CO_2$ to replace oil where appropriate and thereby pave the way for the adoption of a circular carbon economy.

## REDUCING THE CHEMICAL INDUSTRY'S CARBON FOOTPRINT

"In principle, we could even recover $CO_2$ from the atmosphere. But even in a non-fossil energy system, large quantities of $CO_2$ are available from numerous industrial processes. If we could tap into these sources to exploit them as raw materials, we could significantly reduce the carbon footprint of the chemical industry," says the Max Planck researcher.

Turning the greenhouse gas $CO_2$ into a raw material sounds like an elegant way to make the chemical industry less dependent on fossil feedstocks, but it's tricky to implement. That's because $CO_2$ is chemically very lazy – if not to say completely apathetic. In technical terms, the carbon is extremely reluctant to give up the oxygen. Indeed, it's for good reason that fire ex-




***Above*** Greenhouse gas as a raw material: $CO_2$ can react with hydrogen ($H_2$) and other substances to form a variety of products. Catalysis steers these reactions toward the desired substance, and life-cycle analyses ensure that the entire process is more sustainable than a method based on fossil raw materials.

***Below*** $CO_2$ extraction: in principle, it's possible to filter the gas from ambient air and put it to practical use, as Climeworks has shown with this demonstration device.


tinguishers are filled with $CO_2$ in order to fight flames.

At the same time, there's no shortage of substances that bind with oxygen even more readily than carbon – hydrogen being one example. However, you first need to break the carbon-oxygen bond, which takes a considerable amount of energy. "From a climate protection perspective, that's why it makes sense to use $CO_2$ in chemical production particularly if this energy comes from renewable sources," says Walter Leitner. "We're now developing the scientific and technology basis for these new interfaces between energy and chemistry – for example, in the Power-to-X initiative." With Leitner as one of the coordinators, this project is funded by the Federal Ministry of Education and Research (BMBF) and includes partners from academia, industry, and other parts of society.

## TWO AIMS: HIGH-VOLUME AND HIGH-QUALITY PRODUCTS

One approach to chemical production using $CO_2$ begins with the electrolysis of water to produce hydrogen – using sustainable electricity. In future, this could also allow electrical energy to be stored in times of excess supply from wind turbines and solar panels. Then, chemists use catalysts to arrange for a molecular marriage between hydrogen and $CO_2$.

The researchers in Muelheim envisage using this method for synthesis of methanol, formaldehyde, and formic acid – relatively simple substances that are formed when one $CO_2$ molecule reacts with different numbers of hydrogen molecules in each instance. The substances are used on a massive scale in industry as raw materials for a whole host of products, such as plastics, solvents, agrochemicals, or even pharmaceuticals. Methanol is also of interest as a fuel. But Walter Leitner and his team want to go also a step further than that. They want to combine the greenhouse gas and hydrogen with other chemical building blocks to produce polymers or components of drugs directly. "These higher-value products are more competitive than simple building block chemicals in the early stages of a circular carbon economy and are easier to introduce on the market," says Leitner.

Caroline Gebauer is another researcher who believes that this form of $CO_2$ recycling could have a sustainable future in the chemical industry. Gebauer participates in Power-to-X on behalf of BUND (Friends of the Earth Germany) and advises the project with regard to environmental and climate protection. From this perspective, she currently takes a critical view of synthetic fuels, however, when produced from renewable electricity and $CO_2$.

"Using electrical energy to produce hydrogen and then converting that into a synthetic fuel consumes several times more energy than direct electrical use," says Gebauer. "In our view, therefore, it's only feasible in applications such as shipping and aviation, where there is – as yet – no direct electrical alternative." However, Walter Leitner believes there is a promising future also for fuels produced from wind, solar power, and the greenhouse gas $CO_2$. "Such chemical energy vectors allow renewable energies to be transported over large distances and distributed using existing infrastructure," says the researcher. "That will form an essential part of a sustainable global energy system."

Whether it's for a fuel or a plastic, the chemical use of $CO_2$ relies on catalysts that give the mixture of gases a helping hand – and Walter Leitner's team specializes in this area.

Presumably, everyone knows about the catalytic converter in cars, which converts pollutants into harmless substances. In very general terms, catalysts act as the matchmakers in the world of chemistry: they reduce the amount of energy needed for a chemical reaction, steer it in the right direction, and are often instrumental in making a trans-

Graphic: designergold based on a draft from the MPG; photo: Project Management Jülich/Carola Sonnet

Catalysis research for sustainable chemistry: Christophe Werlé (left) and Alexis Bordet are searching for molecular matchmakers that selectively bring $CO_2$ together with other substances, such as hydrogen.

formation possible in the first place. When it comes to using $CO_2$ as a raw material, the catalysts must perform all three of these tasks.

## IT ALL BEGAN WITH A CATALYST FOR FORMIC ACID

Walter Leitner and his team have been researching suitable catalysts for some time – for example, for the production of formic acid. This molecule is formed by combining a $CO_2$ molecule with precisely one hydrogen molecule. Leitner's interest in this reaction did not come about by chance – it was with formic acid that he began his journey into the world of $CO_2$ chemistry while studying for his doctorate at the University of Regensburg. At that time, he was using formic acid as a source of hydrogen for chemical reactions, producing $CO_2$ as a by-product. "I asked myself, purely out of curiosity, whether this process could also be reversed," says the chemist. It turns out that it could – with a molecular catalyst containing the precious metal rhodium as its active center.

The metal center in this type of catalyst increases the chemical reactivity of one or both reaction partners – and the type of metal determines not only the size of this increase but also how much hydrogen the $CO_2$ takes in and what additional partners it incorporates. However, what comes out of this process is also determined by the so-called ligands, which are often complex organic molecules containing phosphorus or nitrogen as points of contact with the metal. The ligands form a defined envelop around the metal center so that, in many cases, the reaction partners can only attach themselves at certain positions relative to one another. Ideally, this leaves them with only one way of reacting – the one the leads to the desired product.

Christophe Werlé, who leads his own working group in Walter Leitner's Department, is searching for catalysts that bring $CO_2$ and hydrogen together in this way. Sometimes his work also involves optimizing an existing catalyst. Here, his first question is always why a catalyst does what it does. In this way, he hopes to identify starting points for improving these chemical facilitators – for example, in order to boost the yield of the desired product and reduce the amount of by-products. But Christophe Werlé also wants to use catalysts as matchmakers in particularly difficult partnerships, such as that of $CO_2$ and hydrogen in formaldehyde.

In practice, this requires a great deal of creativity and, especially, hard work. After all, Christophe Werlé and his team have set their sights on the intermediate products in which the catalyst, as a mediator between the starting materials, forms itself only weak bonds

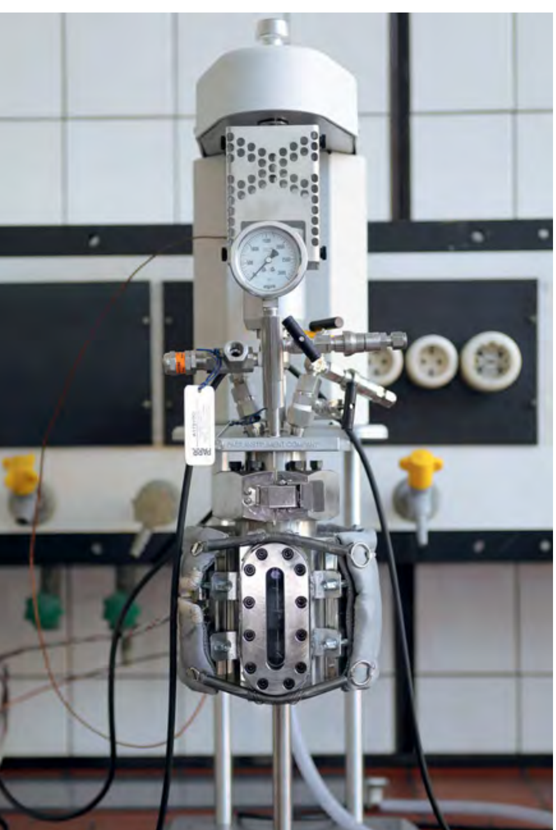
Photo: Thomas Hobirk

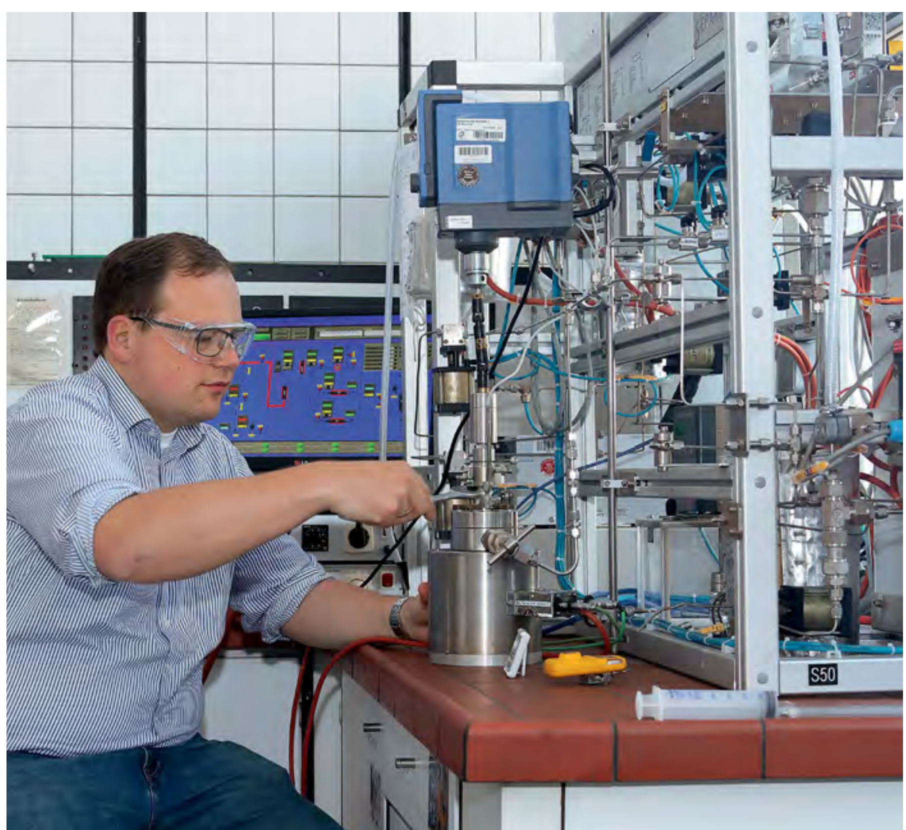
with the partners to be. Based on these short-lived constructs, the scientists can identify the reaction pathways and potential alternative routes. However, the problem with the short lifespan is that the contacts have no sooner formed than they change again. “To allow us to analyze them, we try to stabilize potential intermediate structures by varying the ligands,” says Christophe Werlé.

Experiments like these give the chemists in Muelheim hints as to how $CO_2$ can be turned into the desired products. Recently, a team made up of Leitner’s colleagues in Aachen and Muelheim identified a catalyst that, for the first time, contains the cheap and abundant metal manganese instead of a precious metal and can be used to convert $CO_2$ into methanol.

## PRECIOUS METAL CATALYSTS ARE AS YET MORE EFFICIENT

Although Walter Leitner is pleased with this achievement, he is confident that catalysts containing a precious metal can also be used in chemical production. After all, he says, the ligands in catalysts for $CO_2$ conversion are often at least as expensive as the metal – and precious metal catalysts are still in many cases much more efficient than the alternatives containing cheaper metals such as manganese, iron, or

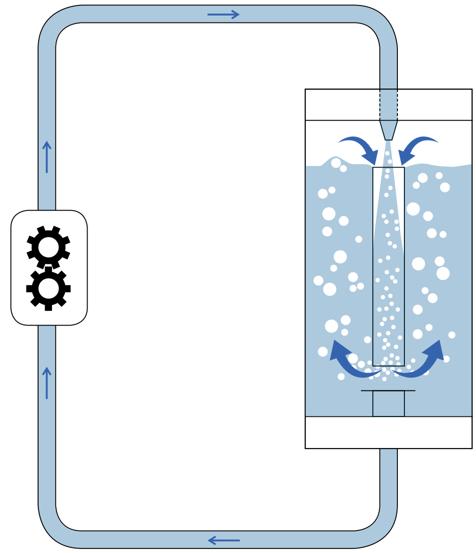





Chemical plant in the lab: using a high-pressure reactor, the researchers in Muelheim study reactions involving gases such as $CO_2$ or hydrogen (left). In this miniature version of an industrial plant, Andreas Vorholt is preparing an experiment to test the long-term stability of a catalyst (right).

Photos: Thomas Hobirk (2)

All mixed up: if the starting materials and catalyst are dissolved in two immiscible liquids, the chemists in Muelheim use a nozzle loop reactor to achieve the closest possible contact between them. Here, part of the reaction medium is drawn off at the base of the reactor and injected back in under high pressure at the top of the vessel. One of the liquids is therefore dispersed in the other as a multitude of small droplets.



nickel. "Even if that only means you can use five percent less of the raw materials in an industrial process, the resulting cost advantage often outweighs that of using a cheaper metal in the catalyst," says Walter Leitner. What's more, another property of catalysts ought to compensate for the downside of using rare and expensive metals: theoretically speaking, they are not used up in the reaction.

## NANOPARTICLES IN A MOLECULAR CARPET

In practice, however, catalysts do wear out over time. This can happen because unwanted substances attach to them, forming persistent impurities, or because the ligands, which are often fragile, become damaged. Molecular catalysts such as those being investigated by the researchers in Muelheim also dissolve in the reaction medium – in what chemists call homogeneous catalysis – and must therefore be laboriously separated out once their job is done.

For this reason, the chemical industry typically prefers heterogeneous catalysis, in which liquid or gaseous starting materials react on the surface of solid catalysts – eliminating the need for a separation process. However, these solid matchmakers are harder to systematically optimize for a chosen reaction. "We're therefore working with scientists from all Departments of our Institute to identify the fundamental common ground between these two areas so that we can enjoy the best of both worlds," Leitner explains.

Alexis Bordet and his team work at the boundary between those two worlds. Instead of individual metal atoms in soluble catalysts, the chemists use metallic nanoparticles and ionic liquids. These substances consist of two charged components, one of which is an organic molecule in the form of a short thread. The scientists in Muelheim chemically attach these molecular threads to a material such as silicon dioxide, producing a charged molecular carpet that attracts the metallic nanoparticles like velour attracts dust. The reaction partners then flow across the chemical pile, which is interspersed with metal atoms, and are paired off while traveling through the reactor.

Here, the team wants the molecular carpet fibers to do more than just hold the nanoparticles in place. "The ionic liquids interact strongly with the nanoparticles and can act as a catalyst themselves," explains Alexis Bordet. "We exploit this behavior to combine different functions of the two components into tailor-made catalysts, which then allow us to transfer the hydrogen to substances from biomass with a high degree of selectivity or to $CO_2$ directly."

While Alexis Bordet is working on catalyst recycling using his "catalytic carpet", Andreas Vorholt is conducting research into engineering solutions with a view to helping industry use dissolved molecular catalysts that have proven effective in the research lab. The chemist, who leads a research group of his own at the Institute in Muelheim, also studied business administration and has previously worked as an advisor to industry. But it wasn't the first time that he realized: "There's a big gap between what academic research makes possible and what industry goes on to implement. That's why we want to provide practical data, so that industry says: that's really good – why don't we try it too?"

## THOROUGH MIXING FOLLOWED BY PERFECT SEPARATION

With this in mind, Andreas Vorholt is focusing on reactions in mixtures of liquids that separate from one another, like oil and vinegar in a salad dressing. In these situations, the catalyst may find itself in an organic liquid, for example, while the product collects in an aqueous solution – or vice versa. But this concept presents chemists with a dilemma: during the reaction, all of the components are supposed to mix thoroughly – and, in the case of $CO_2$ and hydrogen, the process even involves gaseous starting materials. At the same time, the catalyst and the product are supposed to go their strictly separate ways once the reaction is complete. "It's like in real life: you always want exactly what you don't have," says Vorholt. Indeed, it's hard to come by a for-

Graphic: designergold based on a draft by the MPG

*Above* Distilled ideas: Sheetal Sisodiya, Walter Leitner, Christophe Werlé, and Christina Erken (from left) discuss new experiments that can put $CO_2$ to use.

*Below* More climate-friendly in the future: the greenhouse gas can be used as a raw material for foams.

mula in which the reaction partners are fully dissolved in the catalyst solution but the product then fully migrates into the other liquid.

One way out of this awkward situation is for the starting materials and the catalyst to be present separately in the two liquids and for one liquid to then be dispersed throughout the other in the form of extremely small droplets. This provides the future partners with a large contact surface where they can meet the catalyst and react. Andreas Vorholt's team implements this concept using a nozzle loop reactor, in which part of the cocktail is drawn off at the base of the reaction vessel and injected back in under pressure through a nozzle at the top. "This produces fine droplets, and the reaction proceeds much faster than in conventional reactors – even though the catalyst is left totally separate from the product at the end of the process," explains Vorholt.

In order to gain a better understanding of what goes on in their reactors, and to influence the process, the chemists are setting up lab-scale copies of industrial systems and incorporating a whole host of analytical instruments. "We're integrating a working section for online monitoring – because how cool would it be if I knew that the catalyst isn't doing what it's supposed to do right now, and I could then counteract that," says Vorholt.

## $CO_2$ AS RAW MATERIAL FOR MATTRESSES AND SPORTS FLOORS

One current example serves as proof that catalysts and chemical processes can actually be adapted to allow the industrial conversion of $CO_2$. At the CAT Catalytic Center, a joint research center of the company Convestro and Leitner's group at RWTH Aachen University researchers have helped develop a process that can incorporate $CO_2$ into a polyol – a key component of foams and adhesives.

The company aquires the necessary $CO_2$ from other chemical processes, where it arises as a by-product, and uses it to replace a proportion of the starting material for polyol production – which used to be obtained exclusively from petrochemistry. Covestro is now producing the first polyols with a $CO_2$ content of up to 20 percent on the scale of a several thousand tonnes. The process therefore preserves resources and reduces $CO_2$ emissions accordingly, as demonstrated in comprehensive life-cycle analyses conducted by André Bardow, a professor at RWTH Aachen University. Foam whose molecular framework incorporates $CO_2$ is already being used to make mattresses and recently even sports facilities were equipped with flooring based on these materials that contain $CO_2$.

For Walter Leitner, the $CO_2$ mattresses are a perfect showcase – and are therefore just the beginning of some-

Photos: Thomas Hobirk (top), shutterstock (bottom) thing much bigger. Whether the chemical industry ultimately uses this greenhouse gas as a raw material for other products will, however, also depend on factors over which he has no influence with his catalysis research. One example is how efficiently and economically $CO_2$ can be captured when it's formed in large quantities. Moreover, sufficient electricity must be available from renewable sources to produce hydrogen sustainably if it is to partner up with $CO_2$ – and the gases must be made available at the same site before being processed by the chemical industry.

In Caroline Gebauer's view, $CO_2$-based chemical production should receive a bit of help to get started: "$CO_2$ emissions should carry a far higher price – one that takes account of the climate damage associated with it," says the Power-to-X expert from BUND. "A carbon tax would certainly help." Regardless of this, Walter Leitner believes there are good opportunities to put $CO_2$ to use. "Even today, converting $CO_2$ with hydrogen can be beneficial from an environmental and economic perspective, particularly where the existing processes are costly and energy-intensive," says the chemist. But of course, the sustainable processes would be more competitive if the economic assessment took account of the carbon footprint. "In addition to the chemical catalyst, this would then provide the economic catalyst." ◂

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## SUMMARY

- With a view to using $CO_2$ as a raw material in the chemical industry, Max Planck researchers are searching for suitable molecular catalysts and production processes.
- They have already identified chemical matchmakers that combine the greenhouse gas with hydrogen to produce methanol and formic acid.
- To avoid the need to laboriously separate dissolved catalysts from the products after a reaction is complete, chemists use metallic nanoparticles, which they attach to a base material with ionic liquids, or a reactor in which the catalyst and the products are held in different liquids.


## GLOSSARY

**Catalyst:** A substance that reduces the energy needed for a chemical reaction, steers it in a chosen direction, and is often instrumental in making a transformation possible in the first place. The catalyst is not used up in the reaction. In homogeneous catalysis, the starting materials, the product, and the molecular catalysts are all dissolved in one liquid. In heterogeneous catalysis, liquid or gaseous starting materials flow across a solid catalyst instead.

**Ligand:** The building blocks of a molecular catalyst arrange themselves around the metal atom – the active catalytic center – in order to steer the reaction in a chosen direction.

**Power-to-X:** One of the Kopernikus projects, with which the Federal Ministry of Education and Research (BMBF) supports schemes relating to the energy transition. Among other things, Power-to-X investigates the use of energy from renewable sources to produce hydrogen, which is then combined with $CO_2$.