

The image shows a large industrial facility, likely a power plant or refinery, with several tall smokestacks. The central stack is the most prominent, emitting a thick, billowing plume of smoke that fills much of the upper frame. The smoke has a distinct orange or reddish tint, possibly due to the lighting or the nature of the emissions. The sky is a clear, pale blue. The smokestacks themselves are white with dark horizontal bands near the top.

Climate Protection in a Nanosponge

Recycling for waste gases: Researchers at the Fritz Haber Institute hope to stop power stations from pumping carbon dioxide into the atmosphere, where it causes the greenhouse effect. They want to use it to generate fuel or raw materials for the chemical industry.

Three problems, one solution: This is the special charm of a research project on which **Malte Behrens** and **Robert Schlögl** are working at the **Fritz Haber Institute of the Max Planck Society** in Berlin. The chemists want to use carbon dioxide as a chemical raw material, which would keep the greenhouse gas out of the atmosphere, replace coal, gas and oil, and store renewable energy.

TEXT **PETER HERGERSBERG**

This waste is invisible and quite harmless at normal concentrations. It doesn't smell bad or attract vermin, and yet it is a rather nasty form of garbage that humanity needs to grapple with: carbon dioxide. Industry, traffic and private households heat the climate with an extra 35 billion tons of the greenhouse gas every year. One possible solution is to dispose of the gas in underground repositories, although this is very controversial. It would be better to recycle the waste that is generated primarily by burning fossil fuels.

In any case, Malte Behrens and Robert Schlögl, together with their colleagues at the Fritz Haber Institute of the Max Planck Society in Berlin, hope to help turn this colorless, odorless gas into a fuel or a raw material for the chemical industry: methanol or carbon monoxide. Other research groups are working to generate methane or formic acid from the greenhouse gas. Whatever the final substance, carbon dioxide is anything but the ideal reactant, as it is relatively inert – there is a good reason why it is used as a fire extinguisher.

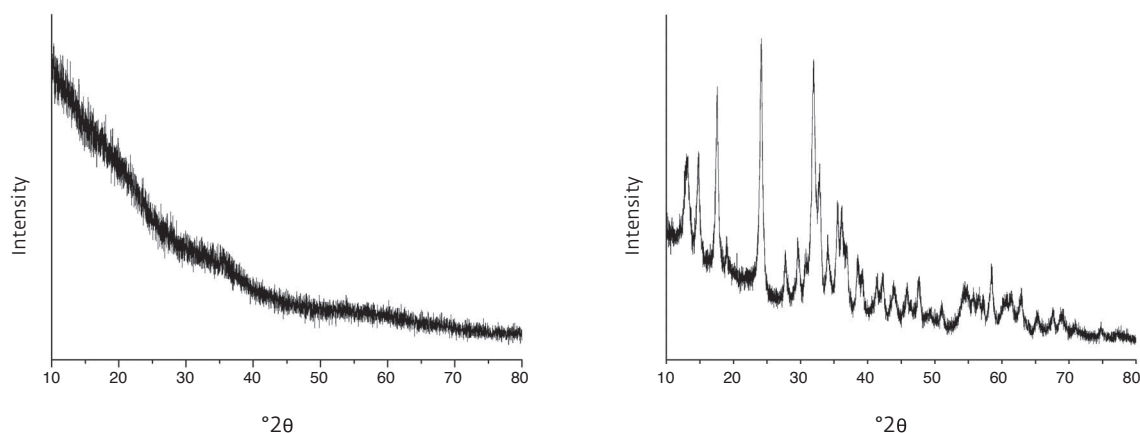
Chemical activation of the gas is also the aim of the CO2RRECT project in which the Berlin-based scientists are

involved. Its name stands for CO₂ Reaction using Regenerative Energies and Catalytic Technologies. The project is sponsored by the German Federal Ministry of Research, and involves four major partners in industry and ten academic research institutions, including the Max Planck Institute for Dynamics of Complex Technical Systems in Magdeburg.

METHANOL AS STORAGE FOR RENEWABLE ENERGY

Using carbon dioxide as a raw material would not only help the climate, but it could also help replace fossil resources. The greenhouse gas could even become a storage medium for chemical energy, advancing the energy transformation. "Unless we solve the storage problem, we won't be able to make the switch to renewable energy," says Robert Schlögl, Director at the Fritz Haber Institute. Since the energy provided by wind turbines and solar panels fluctuates with the wind and the sun, supply seldom matches demand.

Power stations that convert fossil fuels into electricity plan to cover the gap by storing wind and solar energy for times of higher demand. One candidate is hydrogen, which can be ob-



Taking shape with age: At first, the nanoparticles in the precursor have no orderly structure, but are amorphous. They form crystals as they age, as clearly seen in the X-ray diffraction graphs. The amorphous structure delivers no signal, while the crystalline structure yields sharp peaks for some scattering angles ($^{\circ}2\theta$).

tained from water by electrolysis. However, it also has some disadvantages: not only does the gas explode easily, it is also so transient that some is always lost in handling. As a result, it must be compressed and cooled or chemically bound for transport and storage, at considerable expense. Methanol is much better behaved and is easily conveyed from A to B in tanks. Moreover, the alcohol's qualities as an energy source can be used in both fuel cells and internal combustion engines, and methanol-based fuel is already available at some gas pumps.

Scientists working with Liisa Rihko-Struckmann and Kai Sundmacher at the Max Planck Institute for Dynamics of Complex Technical Systems calculated that using methanol in the energy supply equation may be worthwhile. No matter which of the two substances is used to store solar or wind energy, the largest amount of usable energy is lost in the electrolytic production of hydrogen, which is also required for methanol synthesis.

As is always the case when chemically stored energy is put to work, a large amount of heat is generated when hydrogen or methanol drives an engine or fuel cell. The bottom line, however, is that methanol could perform better than hydrogen as a way

station for renewable energy. "The fact is, storing energy in hydrogen is far more difficult and expensive," says Liisa Rihko-Struckmann.

The Magdeburg-based scientist also considers it reasonable to recycle carbon dioxide as carbon monoxide. Carbon monoxide gas is poisonous and not exactly easy to transport, but it shares an advantage with methanol: it is very useful to the chemical industry, as it lends itself to the synthesis of more complex chemical compounds, including synthetic motor fuel.

METHANOL SYNTHESIS WITH PURE CARBON DIOXIDE

In fact, the industry already converts carbon dioxide to methanol on a very large scale, with some 90 factories around the world producing almost 50 million tons of the alcohol in this way every year. Still, the Berlin-based scientists are concentrating on this very question of methanol synthesis. They want to find out whether the established process actually achieves maximum efficiency, and they also hope to optimize the procedure for obtaining carbon dioxide from waste gases.

The industry currently doesn't use the carbon dioxide emitted from the chimneys of coal power stations for

methanol synthesis. Rather, it works mostly with a gas mixture that is specially produced from natural gas or coal, and that contains a considerable amount of carbon monoxide, as well as hydrogen and carbon dioxide. The established processes aren't particularly efficient at converting pure carbon dioxide from coal-fired power stations or the like to methanol. This is mainly due to the catalyst that binds the carbon dioxide to the hydrogen – and it is precisely in the area of this chemical matchmaker, without which little would happen in the chemical industry, that Malte Behrens and Robert Schlögl are experts.

"We are searching for the ideal catalyst for converting pure carbon dioxide to methanol," says Malte Behrens, "and we are doing so using a knowledge-based approach." In other words, the chemists in Berlin want to start by understanding why the mixture of copper, zinc oxide and a small dose of aluminum oxide, which is currently used to convert the carbon dioxide-carbon monoxide mixture, works so well. Trial and error has shown this recipe to be especially effective, but only when it is prepared according to a very precise procedure. The Max Planck scientists are also investigating why this procedure must be adhered to so strictly.

Based on their findings, Malte Behrens and Robert Schlögl then hope to identify chemical matchmakers that will be the ideal mediators for such reactions as methanol synthesis. “We have deliberately selected the example of an established industry process to show that our strategy is successful,” explains Robert Schlögl. It is an ambitious goal, as the chemical industry has already made many efforts to increase the efficiency of the catalyst for methanol synthesis.

MODEL SYSTEMS OVERSIMPLIFY CATALYSTS

However, industrial researchers and developers have not tried what the Berlin scientists propose. “We are convinced that you have to study catalysts in all their complexity,” says Schlögl. To date, chemists have studied the copper-zinc oxide catalyst in simple model systems, such as precisely measured copper islands on a completely smooth zinc oxide surface. The catalyst used in industrial reactors has little to do with this idealized model. The reality is that the reaction mediator used in industry is a sponge-like conglomeration of countless spheres, each measuring ten nanometers (millionths of a millimeter), some of copper and some of zinc oxide, with a small scattering of aluminum oxide.

Until a few years ago, the state of knowledge was that the actual reaction occurred only at the copper spherules. Moreover, chemists long assumed that, to increase the activity of the copper, they need only give it a large surface area – so a sponge of countless nanospheres seemed to be exactly what was called for. For years, textbooks assigned zinc oxide the role of a spacer that pre-



The first step is the most important: Using a semi-automatic precipitation reactor, Julia Neuendorf and Malte Behrens monitor the precipitation of a mixture of copper, zinc and aluminum salts – the precursor of the catalyst for methanol synthesis (top). Stefan Zander uses X-ray diffraction to analyze the structure of the different intermediate products and the finished catalyst (bottom).



How good is the catalyst? Nygil Thomas tests the activity of the catalysts by bringing them together with the reactants under precisely controlled conditions and analyzing the resulting products.

vents the copper particles from fusing with each other in the heat of the reaction, forming larger spheres with a comparatively smaller surface area.

"It has been clear for some time, though, that there's more to zinc oxide," explains Malte Behrens, "because other copper systems with a similar structure exhibit hardly any catalytic activity." So it's not just a question of a large surface. The role of the aluminum oxide also remains unclear. The literature describes it as a promoter, which effectively means something like: "It helps, but we don't really know why."

Malte Behrens and his colleagues are testing many possible catalysts in order to discover why zinc is different from other metals, what factors other than surface area influence the quality of a catalyst, and what part the promoter plays. Sometimes the material mixtures differ in one of their components, and sometimes in a detail of the preparation process, because the procedure holds the key to catalyst research – in both senses. "Many chem-

ists think of the production of industrially relevant solid-state catalysts as a kind of black magic," says Behrens, who plans to demystify the area.

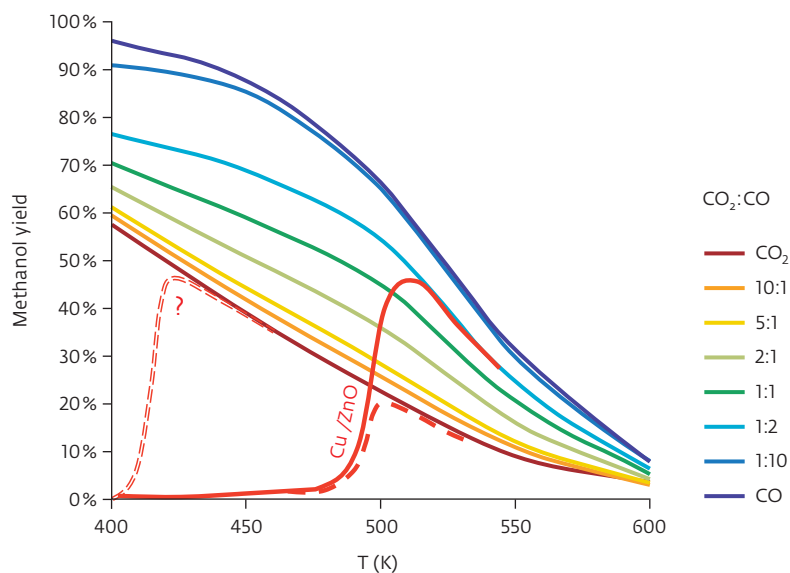
To show how his team goes about its work, he starts in a laboratory where Julia Neuendorf has already prepared an experiment. On the bench stands an apparatus holding a sealed glass vessel at eye level. Inside the vessel, which is as tall as a forearm and just too wide to close two hands around, a mixer stirs a small amount of water. This is where the precursor of the catalyst will be formed – a finely distributed mixture of copper carbonate and zinc carbonate.

THE CATALYST HAS A CHEMICAL MEMORY

Using a number of probes and tubes, a computer monitors the temperature, conductivity and turbidity of the reactor's contents, "but the most important thing is the pH," states Julia Neuendorf. "We have to optimize it for each precursor." This is because the pH

in particular, but also the temperature, influences when the precursor components are precipitated from the solution and what shape their tiny crystals take on, thus also determining the appearance of the final catalyst. "We discovered that the catalyst has a chemical memory," says Malte Behrens. "So it's really important to have a good understanding of the precursor."

On a computer monitor, Julia Neuendorf keeps an eye on all parameters that provide information about what is happening in the semi-automatic precipitation reactor. A pair of colored horizontal lines signals the calm before the experiment. When the doctoral student presses a key, one of the curves falls fast. A blue solution drips into the reactor, and the pH drops into the acid range. The computer immediately triggers the addition of alkaline sodium carbonate and quickly ropes the pH curve in again. At the same time, the solution clouds up with a greenish-blue substance, a mixture of copper carbonate and zinc carbonate.



Job profile of a catalyst for methanol synthesis: In principle, the highest methanol yields are gained by conversion using pure carbon monoxide and hydrogen. The currently used copper-zinc oxide catalyst uses a carbon dioxide-carbon monoxide mixture in the ratio of one to two, but gives very poor yields when pure carbon dioxide is used. The scientists in Berlin are searching for a catalyst that will generate methanol efficiently from pure carbon dioxide at relatively low temperatures, expressed in Kelvin.

As soon as the reactor vessel is full, Neuendorf will filter off the precursor, dry it, heat it and then expose it to hydrogen. Copper oxide and zinc oxide are formed at the heating stage, and the hydrogen releases the oxygen from the copper. Ultimately, the catalyst will have exchanged its malachite green color for an unassuming black. Air no longer agrees with it, because the finely distributed copper would immediately react with the oxygen. The Berlin-based chemists thus take care to keep the catalyst protected from the air while they study it using all the resources of modern catalyst research.

To this end, the catalyst makes a stop in the laboratory of Stefan Zander, who feeds the material through different instruments. X-ray diffraction enables him to determine the crystal structure of the nanoparticles and even to see how it changes as the catalyst does its work. He analyzes the chemical composition using X-ray fluorescence spectroscopy, and has something particularly sophisticated ready for surveying the surface of the finely granulated copper: reactive frontal chromatography. This involves a flow of nitrous oxide, better known as laughing gas, through the porous catalyst.

“Laughing gas is a mild oxidizing agent that deposits precisely a fixed amount of oxygen,” explains Stefan Zander. “We capture the nitrogen that is left over.” The amount of nitrogen tells Zander how much oxygen was chemisorbed onto the copper, and thus the size of the copper surface.

A LOOK AT INDIVIDUAL ATOMS REVEALS THE SECRET

But the true test is actually waiting in the wings where Edward Kunkes and Nygil Thomas work. These chemists test the catalyst at a temperature and pressure that would be used in industry. They feed carbon dioxide and hydrogen through the catalyst and analyze what comes out using gas chromatography.

The catalysts studied by Malte Behrens’ team routinely undergo these tests at the Fritz Haber Institute. However, it was a particularly close look at the catalyst that opened his eyes and those of his international colleagues as to why the combination of copper, zinc oxide and aluminum oxide and their tried and tested production process works better than all the alternatives to date. In the images generated by a high-resolution transmission electron microscope, the scientists made

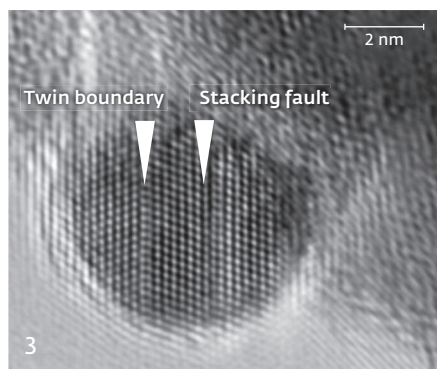
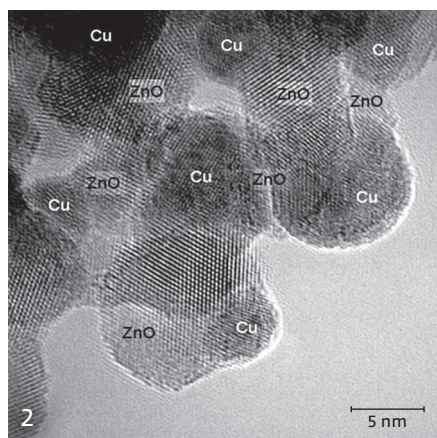
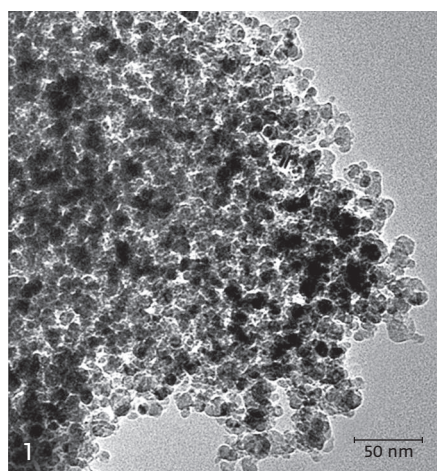
out individual copper and zinc atoms in a small section of the aggregate.

The atomic structure revealed that the catalyst performed properly only when defects were present. Small irregularities in the crystal lattice of the copper particles are expressed on the surface as kinks, notches and barbs, and the reactants and intermediate products of methanol synthesis bind particularly well to these very defects, as team members from Stanford University calculated.

The look at the individual atoms in the copper-zinc oxide sponge also confirmed a suggestion that had been made repeatedly in scientific publications on methanol synthesis: zinc oxide is not only present in nanoparticles that act as spacers between the copper particles; it also spreads over part of the copper, forming a disorderly layer just a few atoms thick. Individual zinc atoms probably even finagle their way into the copper lattice.

“As the calculations by our colleagues from Stanford University showed, the oxygenated intermediate products bind better to the zinc atoms than to the copper atoms,” says Malte Behrens. If the catalyst gives the intermediate products a better grip, they are generated more readily. This means

Close-up of the nanosponge: The tried and tested catalyst for methanol synthesis consists of countless particles comprising copper, zinc oxide and a small proportion of aluminum oxide (1). The copper and zinc oxide particles can be distinguished under the high-resolution transmission electron microscope (2). A look at the arrangement of individual atoms in one particle reveals stacking faults and twin boundaries (3). These defects in the crystal structure are also apparent on the particle surface and increase the activity of the catalyst.



that the catalyst works better overall, because its main function is to generate the unstable chemical structures that inevitably result on the path from reactant to product.

"This leads us to believe that the active areas of the catalyst are where the zinc oxide and the copper defects meet." The team's findings also shed light on the role of aluminum. The triple-charged aluminum ions probably integrate into the double-charged zinc lattice and change its electronic properties, so that the thin layer of zinc oxide lies more loosely on the copper particles.

Since the researchers now know the exact place where the carbon dioxide and hydrogen bond, they can explain why only the industrially established procedure delivers a workable catalyst. The fact is, it is only under those specific temperature and pH conditions that a catalyst precursor forms from which copper crystals with tiny defects and a thin zinc oxide coating are generated in the subsequent stages of the process.

"Our data would indicate that it may be possible to further optimize the tried and tested copper-zinc oxide system," says Malte Behrens. "But I think that, to identify considerably better catalysts for methanol synthesis using pure carbon dioxide, we will have to look at new combinations of materials and new synthesis strategies." Since the scientists in Berlin discovered the secret of the most efficient reaction mediator to date, they know what to look out for.

Even if there's not much that can be changed in the existing copper-zinc oxide system itself, its production pro-

cess can be improved – at least in terms of sustainability. In the current industrial procedure, large amounts of nitrates accrue, and these either overfertilize the water or are processed at considerable expense. "In our experiments with different precursors, however, we found that we can replace the nitrate with ecologically harmless formic acid salts," says Behrens. "This means we can use an environmentally friendly process to generate a catalyst that has the same structure and efficiency as the one that uses the nitrate solution."

CARBON MONOXIDE PRODUCTION WITHOUT PRECIOUS METALS

One of Behrens' suggestions for improving the catalyst that converts inert carbon dioxide into active carbon monoxide goes even further. He recently presented a combination of materials consisting of nickel, magnesium oxide and aluminum oxide. His group had previously completed a detailed analysis of the catalysts generally used in industry. They play their part as chemical mediators quite well – but only thanks to a precious metal component such as rhodium or platinum.

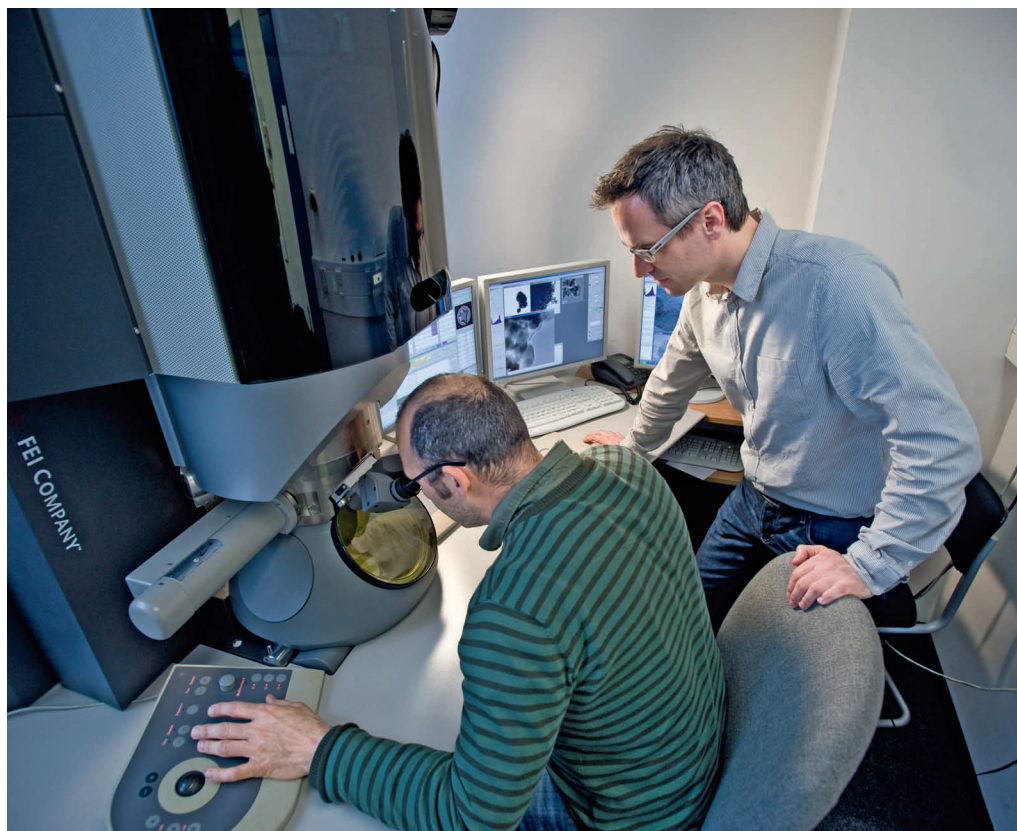
Not only does the material from the Berlin-based laboratories manage without expensive precious metals, it may also permit greater efficiency in carbon monoxide production. After all, it retains its nanostructure even at 1,000 degrees, so it could work at very high temperatures. This would be good for efficiency, as carbon dioxide and hydrogen generate more carbon monoxide as the temperature in the reactor rises. Tests to assess how well the

nickel-based catalyst works at high temperatures are still ongoing. If it proves itself, it could soon replace the competition from precious metals.

As promising as this work is, the catalysts used to convert carbon dioxide into workable compounds pose only a problem of greenhouse gas recycling. Scientists laboring to produce hydrogen by electrolysis also face major challenges. This method virtually hands them the fuel for the conversion of carbon dioxide, but delivers satisfactory efficiency only when expensive iridium or ruthenium dioxide electrodes are used.

These expensive precious metal compounds are unsuitable as catalysts for water splitting on a major scale, and thus for the goal of the CO₂RRECT partners. Malte Behrens' group has also been working on this issue – and is ready with a possible solution. They discovered that a much cheaper composite material comprising manganese oxide and carbon nanotubes is an alternative to the conventional electrodes.

Robert Schlögl hopes to pursue this more economical replacement in Mülheim an der Ruhr, at the Max Planck Institute for Chemical Energy Conversion that is set to emerge from the Max Planck Institute for Bioinorganic Chemistry. Researchers there will tackle fundamental difficulties that arise in the conversion of renewable energy to storable forms, like methanol, and usable forms, like electricity. This is feasible only with the experience that Robert Schlögl has accumulated in catalyst research, because one thing is clear to him: "The problems of energy conversion and storage are catalyst problems." ◀



A high-resolution transmission electron microscope made it possible for Max Planck scientists Malte Behrens (right) and Mark Willinger to look at the individual atoms of the copper-zinc catalyst. In this way, they were able to detect defects in the copper structure and a thin layer of zinc oxide on the copper nanoparticles.

TO THE POINT

- Catalysts convert the greenhouse gas carbon dioxide into methanol or carbon monoxide, which can be used as raw materials for the chemical industry or as liquid fuels.
- The chemical exploitation of carbon dioxide makes it possible to protect the climate, store energy from the wind and sun, and create a replacement for fossil fuels.
- The precursor of a catalyst plays a major role in determining its properties and catalytic activity.
- A precise understanding of catalyst preparation and the catalytic processes enables more environmentally friendly production of catalysts for methanol synthesis, as well as a catalyst without precious metals for generating carbon monoxide.

GLOSSARY

Semi-automatic precipitation reactor: Uses automatic feedback loops to regulate the conditions, especially temperature and pH, under which salts are precipitated from a solution.

pH value: A negative logarithm of the concentration of oxonium ions (protonated water molecules) in a solution. It provides information on whether a solution is acid or alkaline.

Precursor: A substance created when metal salts are precipitated from a solution. It forms a catalyst after passing through a number of intermediate steps, including aging and recrystallization.