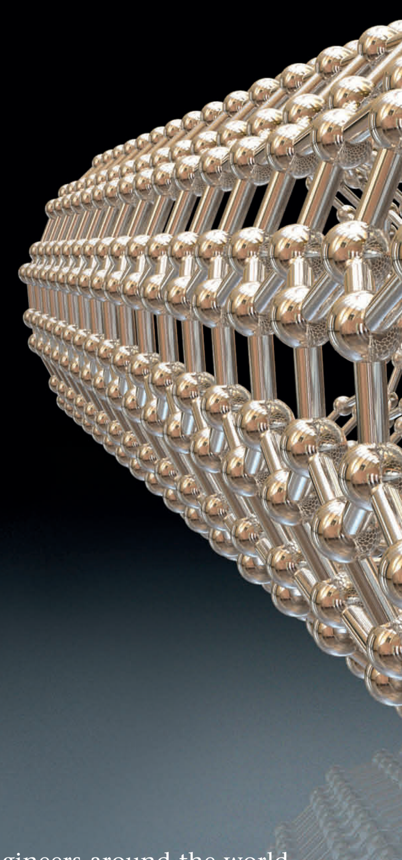
Carbon Acts as a **Chemical Dating Agency**



From plastic bags to hydrogen gas: almost nothing happens in chemistry without catalysts. The reaction accelerators often contain metals that are sometimes rare or need large amounts of energy to do their job. A research team headed by **Robert Schlögl**, Director at the **Fritz Haber Institute of the Max Planck Society** in Berlin, wanted to find out whether it was possible to do without catalysts.

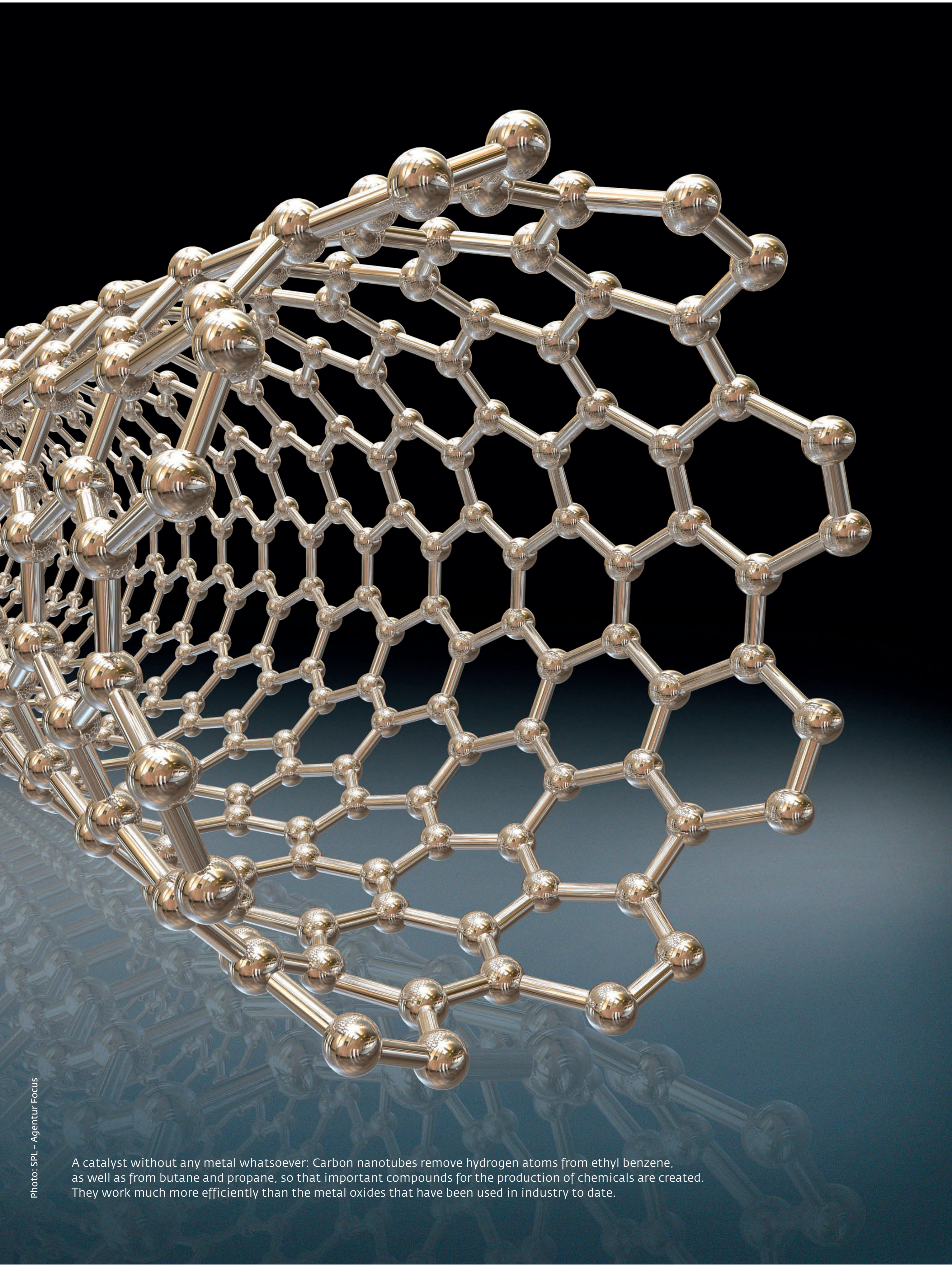
TEXT **STEFAN ALBUS**

Imagine you are standing at the top of the television tower in Berlin. Thousands of people are milling about in the city below, doing their shopping, visiting the Reichstag, going about their business. But it's very foggy – you know all this only from messengers who drop in every now and then. And something else is strange: your sources tell you that people who come to the city as singles sometimes leave as married couples. Others come as a couple and are divorced when they board the Intercity Express to return home. You conclude that, among the thousands who are milling about below, there must be a few very industrious marriage registrars. Your job is to find out precisely who they are.

Crazy idea? Not quite. After all, this challenge is not dissimilar to the one that Robert Schlögl, Director at the Fritz Haber Institute of the Max Planck Society in Berlin, and his team faced a few years back. Strictly speaking, Schlögl's job was even slightly more difficult. And not at all crazy. In fact, it was of quite crucial importance for the chemical industry. "The issue was the synthesis of styrene," explains Professor Schlögl in a sunny office in the institute's high-rise laboratory. "Styrene is an extremely important building block of such plastics as polystyrene and ABS, to name but two. So industry requires around 20 million tons of this monomer every year, which is an enormous amount."

Chemical engineers around the world go to great lengths to be able to pump these 20 million tons of styrene into their reactors. The most important route to this polymer building block runs via a substance called ethyl benzene, from which the engineers remove two hydrogen atoms using a sophisticated process.

Things are not quite so simple in practice, of course, because the ethyl benzene is not prepared to let go of its hydrogen atoms so easily. This is where a so-called catalyst is needed – a compound that loosens firm chemical bonds, beckons oxygen and, at the end of a complex process, marries H and O atoms to each other without changing itself. In other words, a kind



A catalyst without any metal whatsoever: Carbon nanotubes remove hydrogen atoms from ethyl benzene, as well as from butane and propane, so that important compounds for the production of chemicals are created. They work much more efficiently than the metal oxides that have been used in industry to date.

Photo: SPL – Agentur Focus

» Metal-free catalysts would be helpful in using energy more efficiently and developing new energy sources.

All details must be perfect: Pierre Kube follows the catalyst tests very closely. Here, he watches the saturator of the laboratory reactor to observe how a gas dissolves in a liquid.

Photo: Norbert Michalke

of molecular marriage registrar. In oxidative dehydrogenation, this work is usually performed by metal oxides, and the only thing you need to know here is that they are very sensitive. There is a continuous threat of coke formation in the flow of hot ethyl benzene. A useful remedy: hot steam. And a lot of it: for every ton of styrene, engineers must heat up no fewer than ten tons of water, vaporize it and blow it over the catalyst before cooling and recondensing it. "This process uses vast amounts of energy, and thus produces carbon dioxide," says Schlögl, describing his intention. "We wanted to find out whether it couldn't be simplified, so the first thing we did was take a closer look at the catalyst."

And so they did – and got the first sensational result: Schlögl and his team discovered that it isn't the sensitive metal oxide that converts the ethyl benzene into styrene, but a wafer-thin layer of carbon that deposits on the catalyst in the first minutes of the reaction like soot on the wall of a chimney.

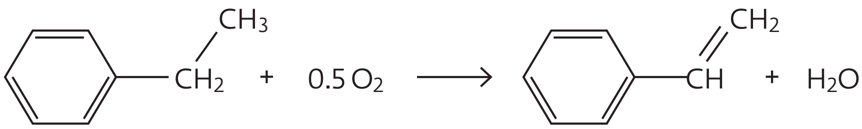
METAL-FREE CATALYSTS WOULD OFTEN BE CHEAPER

This was a real surprise for the chemists: "It took many years before I believed it," Schlögl confesses. "We even tried to refute this initially. It was one of the greatest revelations in my career – to realize that it isn't the metal oxide, but actually the carbon that plays the crucial role in this process!" The revelation meant a completely new opportunity: If carbon does the work, is there any need at all to retain the sensitive metal catalyst below it? Would carbon not do the job on its own? And is it possible to completely forego metals in other catalysts?

Catalysts that don't require metals would be beneficial in many instances. In the case of styrene production, many metalliferous catalysts require great amounts of energy to do their work, and others, like the catalysts used in electrolytic hydrogen production, consist of expensive precious metals. Metal-free catalysts would be helpful in using energy more efficiently and developing new energy sources.

However, the first attempts to dehydrogenate ethyl benzene with the aid of carbon compounds failed – graphite and even diamond simply did not want to do the job. It was time to take a closer look. Schlögl and his colleagues used a large number of extremely sensitive instruments for this. Their first really good lead was provided by a so-called Raman spectrometer. This device detects even slight changes to the surface structure in the scattered light of a laser beam. "The Raman spectrum showed peaks that shouldn't have been there if the carbon was arranged as level as it is on the surface of graphite," explains Schlögl. Instead, the bonds that the atoms formed with each other appeared slightly raised from the plane – the deviation was a mere one degree on average. Nevertheless, it was sufficient to radically alter the character of the surface.

But why was the carbon curved in this way? Probably because, in the styrene hell on a catalyst at a temperature of several hundred degrees, there is simply no time to weave the carbon atoms from the ethyl benzene into the regular hexagonal carpet that chemists call grapheme, and that if stacked one on top of the other, produce graphite; every now and then, a ring closes too quickly and suddenly there is a bulge. Schlögl's colleagues thus looked for carbon compounds that also had a



The formula according to which ethyl benzene is dehydrogenated: It hands over two hydrogen atoms to an oxygen atom, forming water and styrene with a double bond.

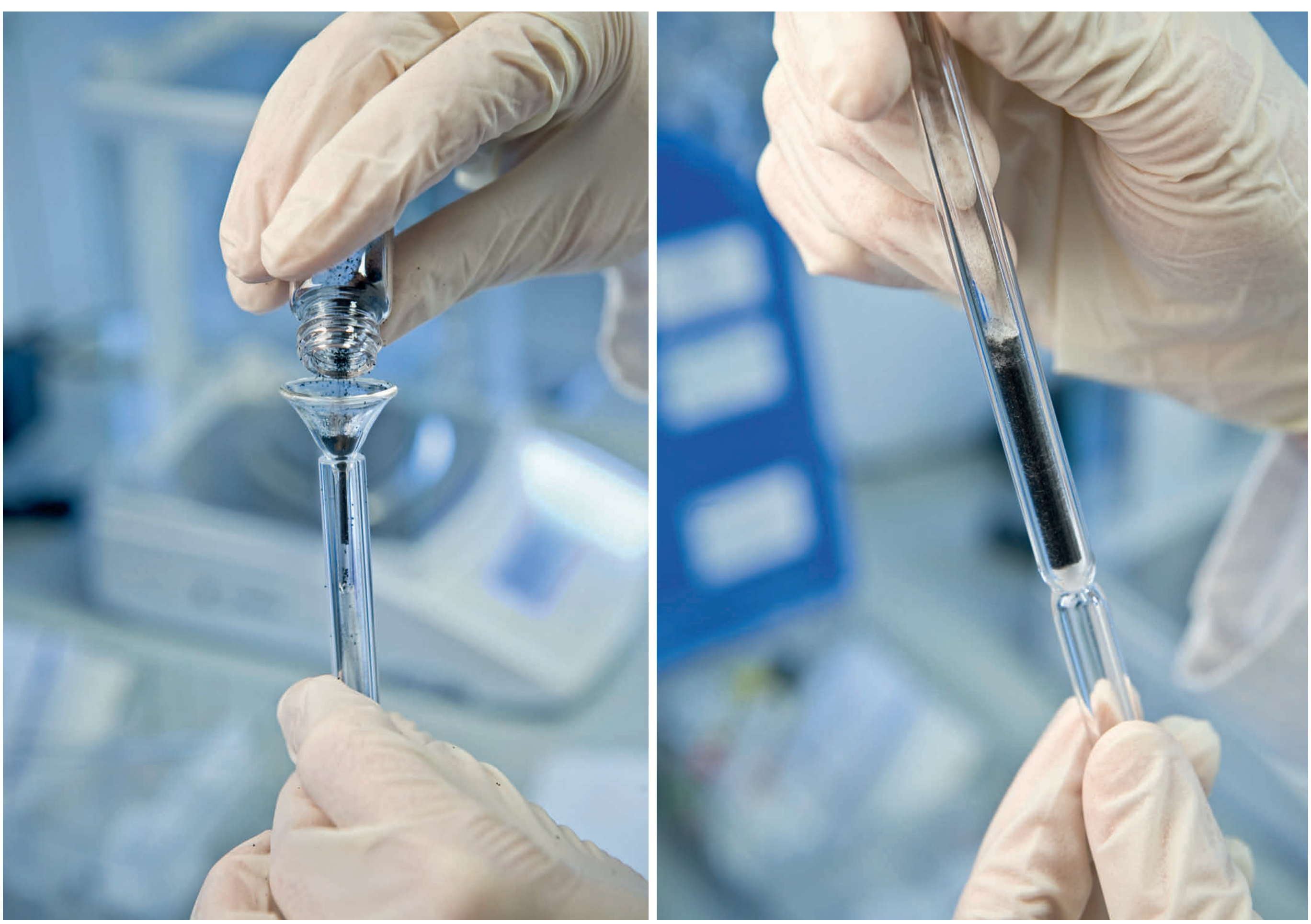
curved surface. The first attempt was again a failure – fullerenes, for example, didn't work.

The scientists got lucky with the so-called *multi-wall nanotubes*, which consist of large numbers of nanotubes stuck one inside the other, a little reminiscent of rolled-up rabbit netting when viewed under a very powerful microscope. The surface of fullerenes has too great a curvature. The curvature of the top carbon layers in the thick multi-wall nanotubes, on the other hand, was just right. This type of nanotube, which is normally used to make plastics conductive, and which industry supplies by the ton, worked! And even better than conventional catalysts, at that. Without hot steam. And, most importantly, "With no metals whatsoever," says Schlögl.

ABSOLUTE CHAOS AS THE REACTION PROCEEDS

But one mystery remained to be solved: How does a slightly rippled carbon surface do things that, until then, were assumed to be the prerogative of complex metal oxides? The decisive clue that put the researchers on the right track this time was the fact that the carbon catalyst always takes a while until the reaction really gets going; and it becomes all the more active the more oxygen it soaks up from the gas flow at the start. These two facts could mean only one thing: "The catalyst is only produced in the course of the reaction!"

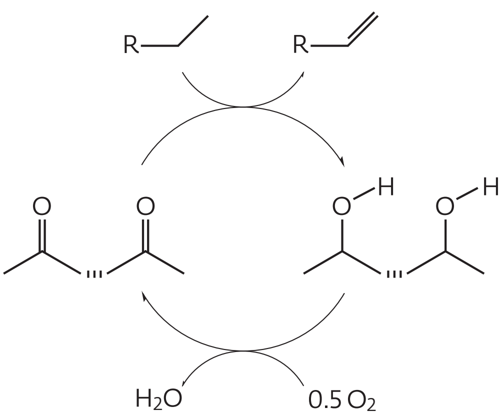
This is the point where Schlögl and his crew suddenly found themselves in the television tower in Berlin, 300 me-

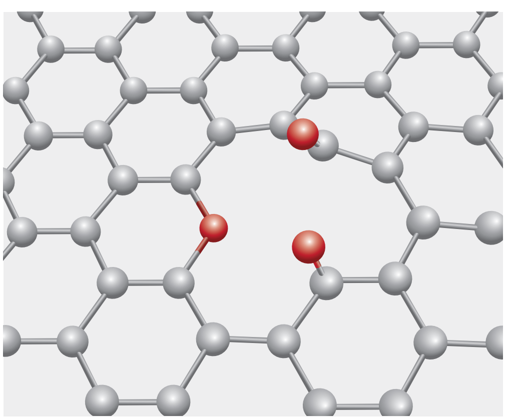


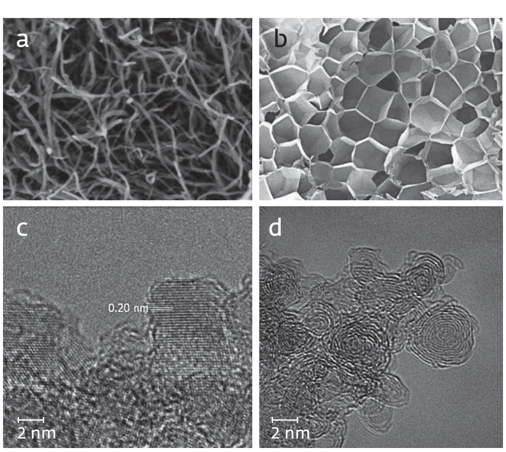
Reactor on a laboratory scale: Carbon nanotubes are filled into a glass tube in order to test their activity. To this end, the researchers guide the reactants into the tube from one side, and analyze at the other end the products and starting materials that weren't converted.

Photos: Norbert Michalke (2); graphic: Fritz Haber Institute – Dang Sheng Su

> The mysterious atomic groups that got the catalyst going turned out to be diketones.







ters above the fogged-in Alexanderplatz – figuratively speaking, of course. Because the things that can be produced from ethyl benzene, styrene and oxygen if these substances are set loose on each other at high temperatures can furrow the brow of any organic chemist: the list comprises almost everything, from acids and alcohols to complex cyclic molecules. And to top it off, they are all swimming in a sea of carbon atoms whose fine structure is somewhere between the carefully-arranged hexagons of pure graphite and the muddle of different atomic combinations that can be found, for example, in coal. Trying to wade through this jumble and find precisely the structure that brings ethyl benzene and oxygen together in just the right way for them to react as desired is like searching for a marriage registrar on the jam-packed Alexanderplatz.

DETECTIVE WORK REVEALS THE ACTIVE COMPOUND

When chemists have to investigate such a muddle, their motto is: quantity counts. Since molecules are so incredibly minuscule, analysts need huge quantities of them to find out more. In addition, the complete reaction in the styrene reactor happens on the wafer-thin surface of a solid body. Its atoms account for only a tiny fraction of the catalytic grains that could be put under a measuring device. Although a liter of water with a drop of oil is, first and foremost, water, it is the oil film that gives it its taste.

The fact that Schlögl's team ultimately succeeded in discovering the catalytically active carbon compound in this jumble is really a feat of detective work. “We simply tried to exclude all the possibilities one by one. What finally remained had to be the ‘guilty party’,” explains the chemist. In other words, he and his colleagues used methods precisely adapted to each particular case to remove carboxylic acids, phenol, lactone and anything else that could be found in the chaos on the catalyst's surface. Overall, they made a foray through classic organic wet chemistry – under more stringent conditions, as the researchers had to work under extremely clean conditions to avoid introducing new impurities into their substrate with their reagents. And to ensure that they removed only the desired class of compounds without affecting others. All in all, it was around eight years of work.

The result, however, was another surprise for everyone: the mysterious atomic groups that got the catalyst going turned out to be diketones – compounds in which two adjacent carbon atoms are each connected to an oxygen atom via a double bond. Although these groups of atoms, also known as quinones, are well known in organic chemistry, the fact “that they are produced under these reaction conditions can't be found in any textbook,” says a still-marveling Schlögl. Moreover, two adjacent oxygen atoms are permanently on call, so to speak, at a carbon seam at a temperature of more than 400 degrees Celsius. There is a risk that they will simply convert into carbon dioxide. But only a very small number of active centers are needed for a good catalyst to get a reaction going; if these are then also constantly reformed from the flow of material, even chemical mayflies will lead to success.

The key is that quinones have a very special trick up their sleeves. Under certain conditions, the two oxygen atoms

Painstaking discovery: Quinones with adjacent oxygen atoms (in center image, red) are catalytically active during dehydrogenation. These pick off hydrogen from the starting compound – a double bond is formed. Oxygen reactivates the catalyst. As catalysts, the Berlin researchers tested a) carbon nanotubes, b) porous carbon from popcorn, c) nanodiamonds, d) onion-shaped carbon (bottom image).

The search for metal-free catalysts: Robert Schlögl (center), Sylvia Reiche and Pierre Kube are looking for chemical matchmakers that bring together molecules without the aid of a metal. They have already chalked up their first successes.

Photo: Norbert Michalke

can exchange their electrons with each other like water in two communicating tubes – what chemists refer to as a quinone-hydroquinone redox pair. This makes the electrons sufficiently mobile to catch the hydrogen atoms of the ethyl benzene while still being able to back away again if the hydrogen atoms are to be surrendered to a passing oxygen molecule: an ability that, until now, had been credited more to metal atoms and their oxygen compounds.

Suddenly, everything fit together: for example, the strange observation that the speed of the styrene formation was dominated by the speed with which the catalyst combusts the stolen hydrogen atoms with oxygen to form water. “Until then, everyone believed it was the hydrogen abstraction that is crucial – which is also what the textbooks say,” recalls Schlögl. But this fits with quinones: they are very good at holding on to water molecules. The speed of the reaction thus depends on how fast a water molecule can free itself from the oxygen pincers of the quinone and make room for two new hydrogen atoms of the ethyl benzene.

SYNTHETIC QUINONE PROVIDES THE FINAL PROOF

The final proof for the catalyst ideas of the researchers in Berlin was then provided by a substance they had recently developed in collaboration with Klaus Müllen’s research group from the Max Planck Institute for Polymer Research in Mainz: practically a miniature section of the curved carbon surface including quinone groupings – and “tremendously active.”

Yet there was still a long way to go from this discovery into the reactors of interested styrene producers. It was important to immobilize the dusty nanotubes, for example, so that they can be easily poured into the reactor as a granulate and not endanger the staff working there – another job that took several years to complete.

But the goal seemed worth it because, as it turned out, the metal-free carbon catalyst was not only exciting from the point of view of a scientist engaged in basic research, but it was also the better alternative to the familiar metal catalysts in several respects. Not only because it works at around 400 instead of 600 degrees Celsius, but because industry can actually save the energy the conventional method needs to heat the vast amounts of steam. “The new method is simply more sustainable,” says Schlögl.

In addition, it reduces the problems resulting from the fact that the catalysts used thus far not only catch ethyl benzene, but also styrene, which they combine with steam to produce further compounds that the engineers must then laboriously filter out. This is where Schlögl’s versions are much tamer: “The carbon surface is hydrophobic,” says Professor Schlögl. “So it isn’t an attractive location for the steam to bond.” This means that Schlögl’s carbon catalysts can also convert other hydrocarbons into valuable products, where metal oxides often miss the mark: propane into the polypropylene component propene and butane into butadiene – a component used by the chemical industry to produce millions of tons of rubber for tires every year, for example.

THE FIRST FACTORY TO USE NANOTUBES IS IN CHINA

First, however, catalysts similar to those developed in Berlin are being used as planned for styrene production – in China. There, oxygen and ethyl benzene are already rushing over around 100 kilograms of catalytically active nanotubes in a pilot plant – and helping engineers in the Far East improve their carbon footprint.

In the meantime, the search for metal-free catalysts continues, not only in Berlin. Robert Schlögl and his colleagues discovered that graphite produces a carboxylic acid from an aldehyde. Metal catalysts can sometimes be replaced with compounds of carbon and other elements, such as nitrogen. Nitrogen atoms in the carbon network of the nanotubes make them even more active as catalysts. Chinese researchers are testing such carbon tubes interspersed with nitrogen as electrode material in electrolytic cells that decompose water into hydrogen and oxygen. To date, precious metal electrodes have been required for this task.

Researchers working with Markus Antonietti, Director at the Max Planck Institute for Colloids and Interfaces in Potsdam, have, in the meantime, presented a catalyst that produces hydrogen directly from water with the aid of light. The photocatalytic material, which has a structure similar to graphite, consists of a network whose nodes are occupied by nitrogen and carbon atoms in turn. This carbon nitride could make one stage of the conventional electrolytic hydrogen production superfluous – when the light energy is first photovoltaically converted into electricity.

Carbon and mixtures of carbon and nitrogen are thus able to replace metalliferous catalysts. Making the materials fit for this purpose is a real task of basic research, and one to which the Max Planck chemists will continue to devote their work. They are assisted in this task by what they have learned in their search for the precise location where ethyl benzene loses its two hydrogen atoms, "because now we really know the details of the chemistry of carbon surfaces well," says Schlögl. ◀

The laboratory reactor is well shielded against external influences, as Pierre Kube must accurately control the conditions of the catalyst tests to ensure that they are comparable.

Photo: Norbert Michalke

TO THE POINT

- **Most industrially relevant catalysts contain metals that are often rare or need large amounts of energy to do their job.**
- **During the dehydrogenation of ethyl benzene to styrene, the actual reaction takes place, not on the metal oxides used as catalysts in industry, but on quinones, which form in a carbon layer above the oxide.**
- **Synthetic quinones produce styrene with higher yields and lower energy consumption than metal oxides.**
- **Metal-free catalysts from carbon or combinations of carbon and nitrogen are also suitable for hydrogen production by electrolysis or photochemical water decomposition.**

GLOSSARY

ABS: A polymer produced from acrylonitrile, butadiene and styrene and used in automobiles, for example.

Dehydrogenation: Hydrogen is removed from a molecule.

Electrolysis: Electrical energy forces a chemical reaction. The reaction takes place in two partial reactions at two electrodes. In one of the partial reactions, a reactant accepts electrons, and in the other, a partner releases electrons, although this is energetically unfavorable. An example is the electrolysis of water to form hydrogen and oxygen.

Fullerenes: Spherical molecules of pure carbon. The best known example is the Buckminster fullerene, which consists of 60 carbon atoms and, like a conventional soccer ball, is composed of 12 pentagons and 20 hexagons.