A FANTASTIC SHORTCUT

“It’s not necessarily a bad thing if you don’t try to directly achieve extremely challenging targets”

ROBERT FRANKE, HEAD OF HYDROFORMYLATION RESEARCH AT EVONIK

The more efficient reactions are, the more sustainable chemistry becomes. Working together with partners from the Leibniz Institute for Catalysis, a group of researchers at Evonik have recently achieved a notable feat—the direct production of the important industrial chemical adipic acid. This breakthrough was even showcased in an article in the journal *Science*

TEXT **KARL HÜBNER** ILLUSTRATION **SAMY LOEWE**

It’s been more than 60 years since Schalke 04 won Germany’s soccer championship. That was back in 1958, when Professor Robert Franke had not even been born. However, as a Schalke fan, Franke dreams of seeing the team becoming the German champion once again. Franke also has dreams as a researcher. Among other things, he would like to carry out some chemical reactions that no lab on earth has managed to achieve to date. Some of these reactions are as unrealistic as the likelihood that Schalke’s neighboring team, VfL Bochum, which is in the second league, could soon become the German champion. Other reactions are at least conceivable—and about as likely as Schalke becoming champion.

Chemists really do refer to them as “dream reactions.” For one of these reactions, Franke recently achieved a breakthrough in cooperation with partners from the Leibniz Institute for Catalysis (LIKAT) in Rostock. The dream of achieving this reaction is about as old as that of Schalke fans regarding their team’s championship, because the literature concerning such research extends back to the 1950s.

The aim is to directly convert butadiene into adipic acid. The latter is a dicarboxylic acid and an important starting material for many other products (see the box on page 56) such as nylon. Several million tons of adipic acid are produced worldwide each year. To date, manufacturers have only been able to produce it by way of several chemical detours and the use of aggressive chemicals such as nitric acid. Moreover, they have to →

“We’re delighted whenever we can apply our academic research to concrete examples from industrial operations”

MATTHIAS BELLER, DIRECTOR OF THE LEIBNIZ INSTITUTE FOR CATALYSIS (LIKAT)

deal with the byproduct nitrous oxide, a molecule that is around 300 times more damaging to the climate than carbon dioxide. It would therefore be much more sustainable if adipic acid could be produced from butadiene in a single step. So it’s no wonder that the recently achieved breakthrough even had an article devoted to it in the renowned journal *Science*.

When chemists write out the equation for this reaction, it looks pretty simple: A carboxyl group (COOH) is attached to each end of a butadiene molecule. The result is adipic acid. In practice, things aren’t quite so easy. That has been demonstrated by the many attempts made in past decades that at best achieved no more than partial success. “One problem is the many possible side reactions, which produce other, unwanted substances,” says Franke. Another obstacle is that the attachment of each COOH group occurs in two separate steps, which to date have only been achieved independently of one another. “As a result, you need to laboriously separate and purify the substances in a variety of steps. This makes the whole thing rather uneconomical,” states Franke.

As is often the case in chemistry, the recent breakthrough was achieved by means of a suitable catalyst. “We couldn’t have done it without the help of the colleagues at LIKAT,” adds Franke. This joint success isn’t the first in the 23-year partnership between LIKAT and Evonik. The two partners have already transferred eight jointly developed processes to technology-center scale and registered more than 140 patents. For many years, they have also been sending staff members to each other on temporary assignments so that they can benefit from one another’s expertise. “It’s a very fruitful partnership,” says Franke.

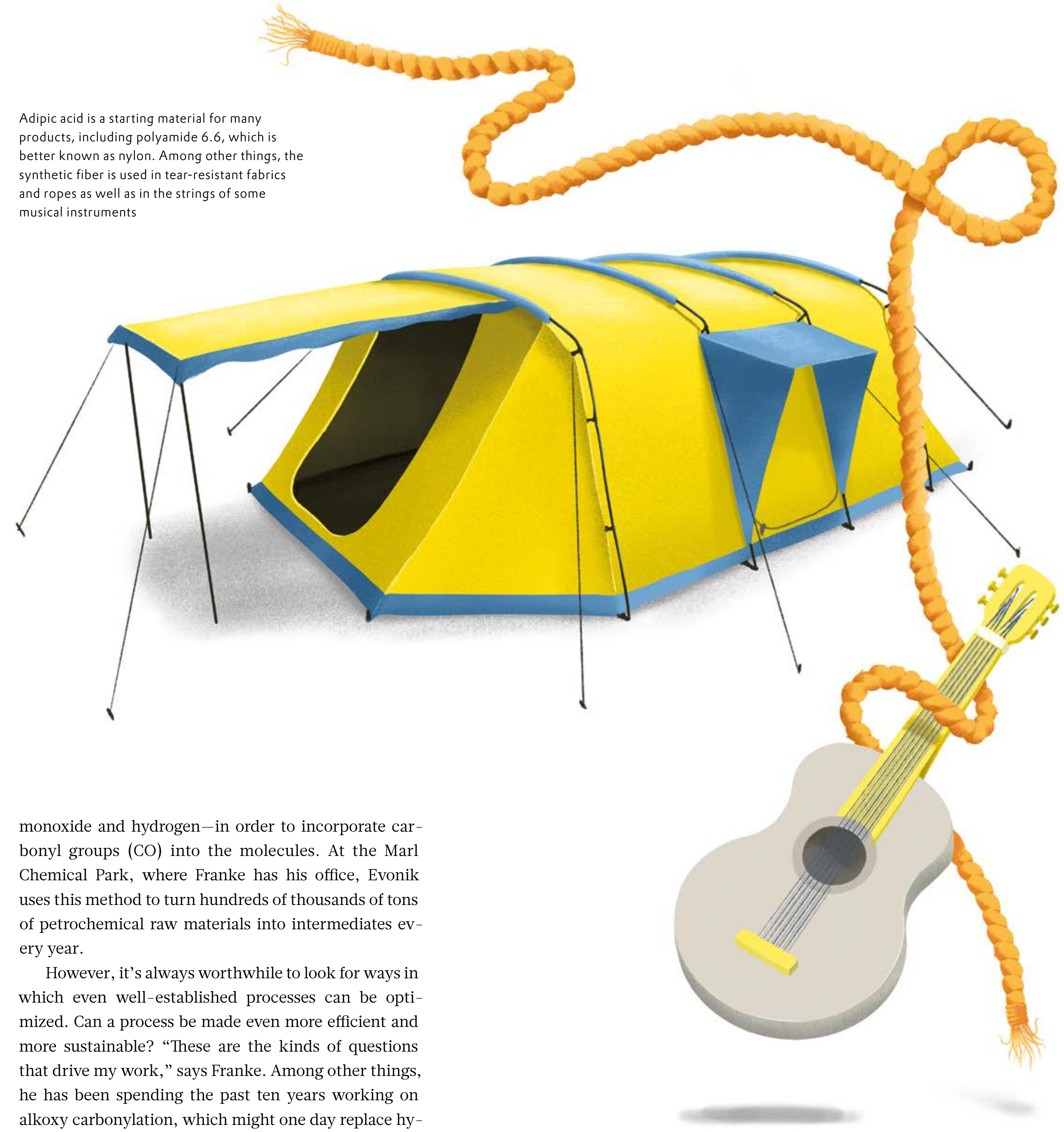
AN ACCIDENTAL BYPRODUCT

However, it’s rather unusual that Franke, as an industrial researcher, is interested in adipic acid, given that it hasn’t previously played a role at Evonik. Franke likes to call such side trips “serendipitous,” which means that the discovery was important but not aimed for. It’s an accidental byproduct.

“It’s not necessarily a bad thing if you don’t try to directly achieve extremely challenging targets but still keep them in the back of your mind,” he says. Dream reactions such as the one that converts butadiene into adipic acid are something that an industrial chemist always has at the back of his or her mind. And at some point a few years ago, the time eventually came for Franke to remember the idea and make his own attempt.

The reason for this was that the hydroformylation research that Franke heads at Evonik had achieved a breakthrough. Hydroformylation is a tried and tested method for reacting unsaturated hydrocarbons, known as olefins, with synthesis gas—a mixture of carbon monoxide and hydrogen—in order to incorporate carbonyl groups (CO) into the molecules. At the Marl Chemical Park, where Franke has his office, Evonik uses this method to turn hundreds of thousands of tons of petrochemical raw materials into intermediates every year.

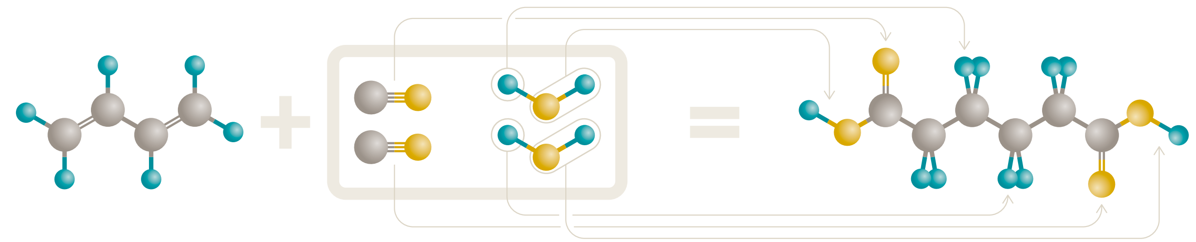
Adipic acid is a starting material for many products, including polyamide 6.6, which is better known as nylon. Among other things, the synthetic fiber is used in tear-resistant fabrics and ropes as well as in the strings of some musical instruments



However, it’s always worthwhile to look for ways in which even well-established processes can be optimized. Can a process be made even more efficient and more sustainable? “These are the kinds of questions that drive my work,” says Franke. Among other things, he has been spending the past ten years working on alkoxy carbonylation, which might one day replace hydroformylation. In this process, the olefins’ double bonds are treated with a mixture of carbon monoxide and an alcohol. This results in esters. Because many products of hydroformylation are converted into esters for later use, the ability to synthesize them directly would be elegant as well as sustainable.

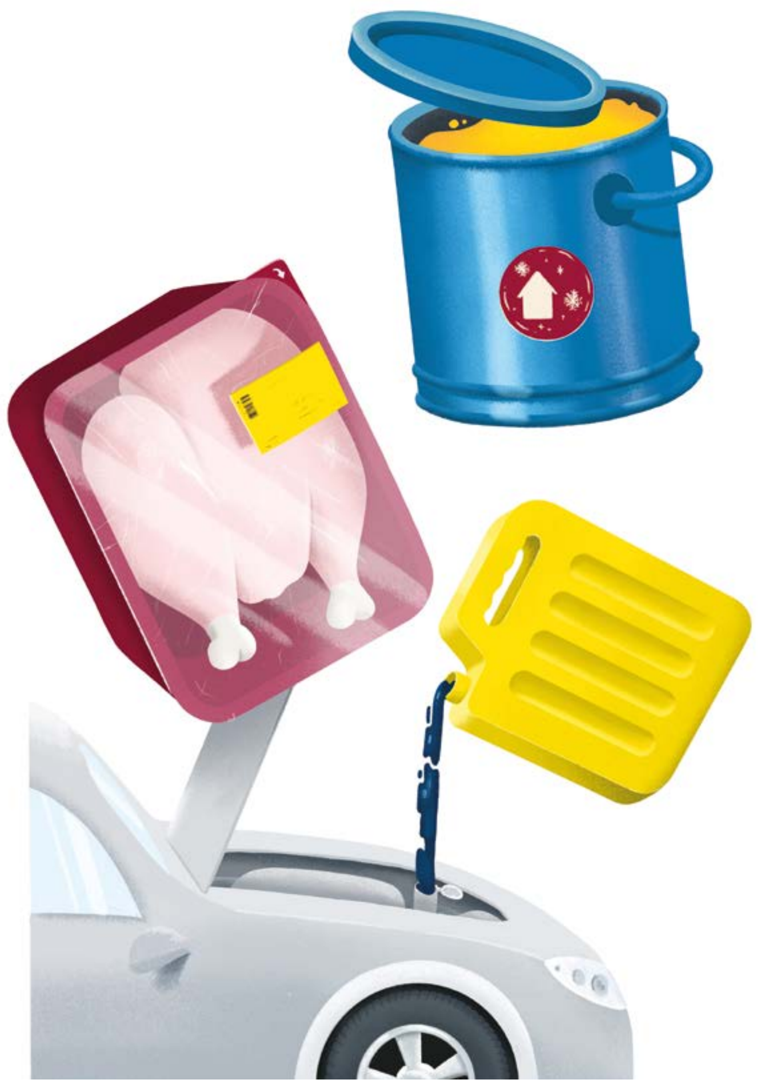
LOOKING FOR A “MATCHMAKER”

One of the biggest challenges that the researchers faced was the search for a suitable catalyst. Catalysts are often referred to as “chemical matchmakers” because they bring molecules together and help to overcome existing energy barriers. Catalysts are often complex molecules that perform a variety of tasks. For example, the planned alkoxy carbonylation of an olefin goes through four to five transition states. The catalyst has to support the process at each transition. As a result, Evonik launched another partnership with the specialists at LIKAT in 2015. The institute’s director, Professor Matthias Beller, immediately agreed. “We’re delighted whenever we can apply our academic research to concrete examples from industrial operations,” he says. →



An acid for many uses

Adipic acid is an important intermediate for the chemical industry, which produces several million tons of it every year. By far the biggest portion of the output is used to produce polyamide 6.6 (nylon), which is turned into fibers for lightweight fabrics that are tear and abrasion-resistant as well as into strings for plucked instruments, tennis racket strings, and wear-resistant parts such as cogwheels. In addition, adipic acid is used as a raw material for certain polyurethanes, which are found in ski boots, sports shoe soles, golf balls, foams, coatings, and adhesives, for example. Adipic acid is also used to produce plasticizers for cables, hoses, foils, and food packaging made of PVC. Other applications include the use in additives that make paints and coatings resistant to low temperatures and as components of lubricants. Adipic acid itself is also approved for use as an acidulant in food (E355). The name is based on the Latin word *adipes* (animal fats). Adipic acid used to be produced by oxidyzing fat. This natural starting material was later replaced by petroleum-based raw materials. Until now, its synthesis required several steps. In the recently achieved reaction, researchers succeeded in producing adipic acid directly from butadiene for the first time. The scientists accomplished this using a catalyst they had developed specifically for this purpose. In the new process, carbon monoxide and water are used to attach two carboxyl groups to a butadiene molecule in a single process step.



Esters of adipic acid are used, for example, as plasticizers in PVC food packaging and as additives in coatings and lubricants

For its starting point, Beller's team chose a catalyst that is well-established in industry, but unsuitable for Evonik's purposes. The specialists at LIKAT changed molecular groups in such a way that the reaction's second stage, the addition of the alcohol, can proceed more rapidly. The team headed by Franke and Beller published this breakthrough in 2017. Thanks to the new catalyst, monounsaturated olefins can be converted into esters with a good yield. Evonik is now preparing the first conversions to the new process on a commercial scale.

This success automatically brought Robert Franke's dream reaction back to mind—serendipitously. The question was: Could the catalyst also work with butadiene? After all, that process also involves a carbonylation, although it has to incorporate not one but two CO groups.

And lo and behold, it worked quite well. However, it produced too many interfering byproducts. The researchers wanted to improve this unsatisfactory selectivity, so to this end they then combined molecular groups from the industrially well-established system with their new candidate. This led to the breakthrough.

Science published the findings shortly before Christmas 2019. It added a one-page expert commentary that stated that the selectivity and product yield of the process were outstanding.

However, the reaction still had one minor drawback: It initially "only" produced an ester of adipic acid. Water had to be added to create the acid itself. Adipic acid could only be produced in one go if water could be used for the reaction instead of alcohol. Although this was difficult at first, the team has also made progress in this regard. "A different solvent enables us to achieve that as well," says Matthias Beller about the follow-on success, which has not yet been published.

However, this result is not yet adequate for industrial applications. "The synthesis of the catalyst is very complicated and uneconomical as well," says Franke. In addition, parts of the complex molecule decompose during the process. Beller's team in Rostock is currently working on developing a similarly effective catalyst that would be easier to produce and more stable.

FROM THE LAB TO LARGE-SCALE TECHNOLOGICAL APPLICATIONS

At the same time as it is enhancing the catalyst, Franke's Evonik team is also working on transferring the reaction to large-scale technological applications. To date, the tests have only been conducted on the laboratory scale, with only a few hundred grams of the various substances. The next stage will take place in a mini plant in order to determine whether the process is permanently stable in such a reactor, says Franke.

At some point, Evonik will decide whether it should produce adipic acid itself or market the process in other ways. The most important raw material for this process, butadiene, would be supplied by the company's own C4 production network at the Marl location. This production network is based on C4 hydrocarbons from petroleum cracking. The name "C4" refers to the fact that these hydrocarbons contain four carbon atoms. Butadiene is one such hydrocarbon.

No matter who uses this process one day, it will make the production of adipic acid simpler and, above all, more sustainable. It avoids "ugly chemistry" (Franke) and all of the starting substances end up completely incorporated into the product, so no waste is produced. In the future, some of the starting materials could also be produced from renewable resources. An example of this is the synthesis gas, from which the carbon monoxide is separated for the production of adipic acid. According to Franke, at least it would allow two of the six carbon atoms in the end product to be created in a green manner.

As a result, the dream reaction has almost become a reality. It would be a great feat if the success in the laboratory could be turned into a large-scale process that replaces the conventional process for producing adipic acid. Robert Franke would be so thrilled that he could even get over it if it took a while for Schalke to become Germany's soccer champion again.

Adipic acid is also used during the production of certain thermoplastic polyurethanes from which ski boots, skateboard wheels, animal eartags, and other items are made