A BRIGHT SPOT FOR THE CLIMATE

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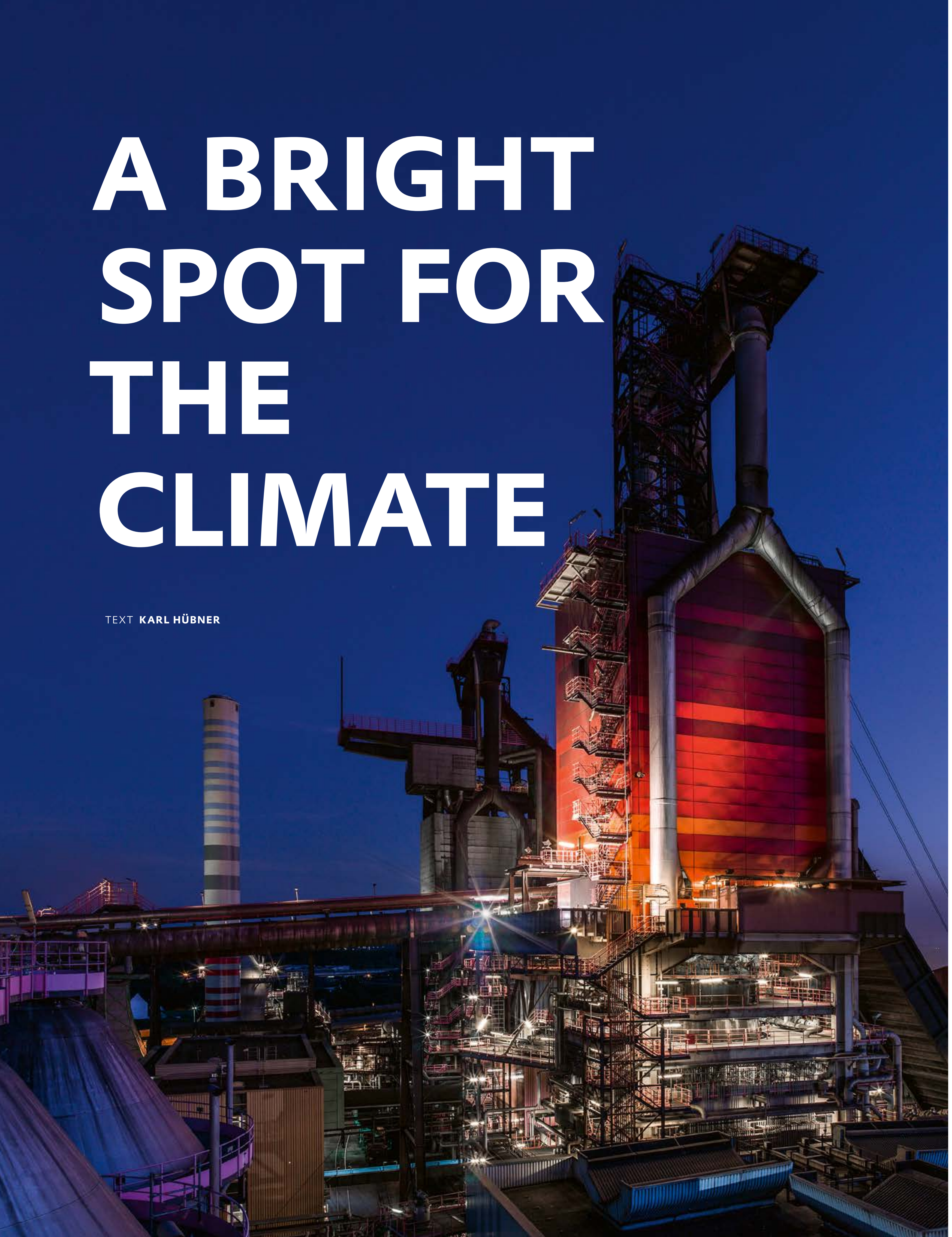


A thyssenkrupp blast furnace in Duisburg at night: Steel production generates carbon monoxide, carbon dioxide, and hydrogen, which could be used in the future for the sustainable production of chemicals

Using the emissions of the steel industry to produce plastics: That's the long-term goal of Evonik and its partners in the collaborative project Carbon2Chem. To reach this goal, they are working with higher alcohols such as ethanol—and catalysts that are being developed in Hanau

The night sky above the Ruhr district no longer glows as brightly as it used to. But when the blast furnace at the steelworks in Duisburg is tapped, it can still be seen from afar. This is where thyssenkrupp produces about ten million tons of steel annually. The smelting process, which extracts the oxygen from iron ore with the help of coking coal, generates huge volumes of smelter gas.

This mixture of gases consists of 40 percent nitrogen, as well as carbon dioxide (CO_2), carbon monoxide (CO), and hydrogen (H_2). Smelter gas is already used today as an important raw material for the generation of energy. By burning the smelter gas, thyssenkrupp generates enough heat to completely cover the Duisburg plant's energy needs. However, the plant still emits 20 million tons of carbon dioxide annually. This accounts for about 2.5 percent of Germany's CO_2 emissions. About eight percent of the world's carbon dioxide emissions are generated by steel production.

That's why the research project Carbon2Chem, in which Evonik is participating, is searching for ways to use carbon and other components of smelter gas to produce chemicals. The project's goal is clear: The more effectively smelter gas is recovered, the lower will be the levels of CO_2 emissions and of the fossil raw materials needed for production.

The project has a broad foundation. In addition to thyssenkrupp and Evonik, the Carbon2Chem project partners include almost 20 companies from the chemical, energy, and steel sectors as well as academic research institutes. The German Federal Ministry of Education and Research is funding the project with about €140 million in total. The first phase of the project began in 2016 and was concluded with promising results. The second phase is now beginning (see the box on page 43).

PROVEN TECHNOLOGY, NEW CHALLENGES

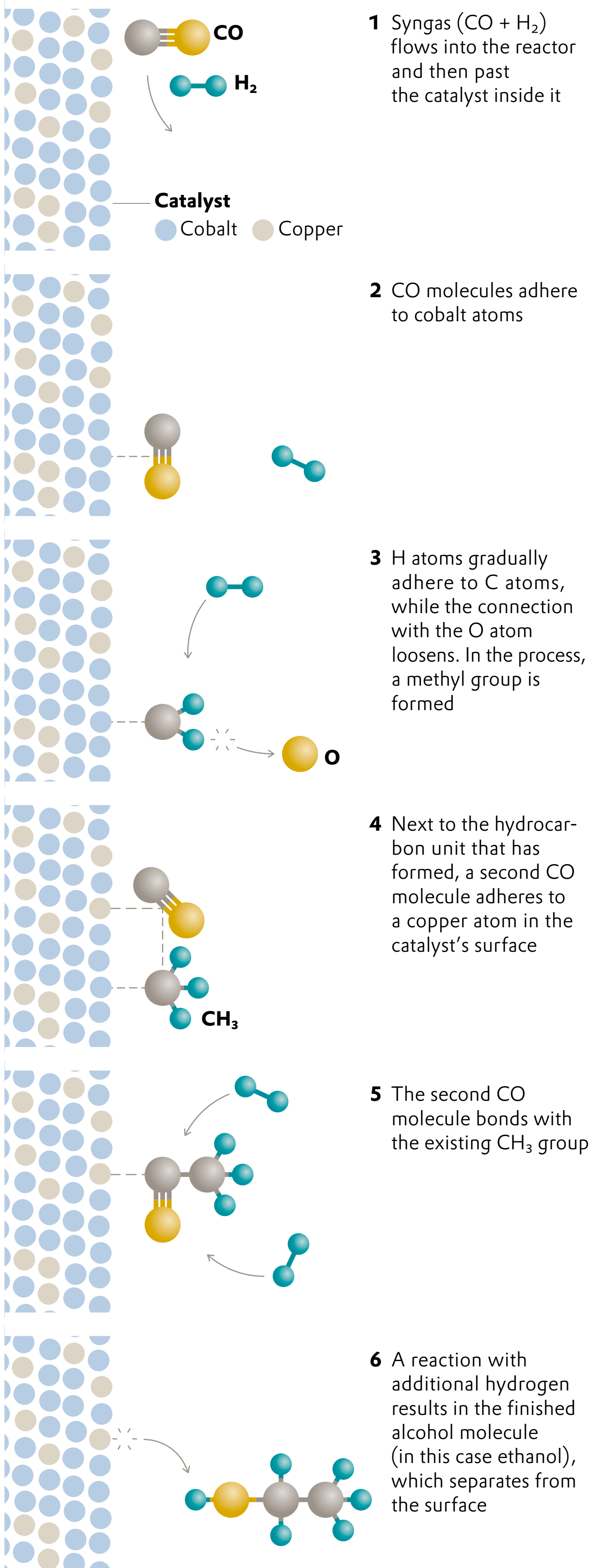
The chemical principles underlying the transformation of smelter gas into a multitude of chemicals have been well known for over a century. The chemical industry has long been using gas mixtures consisting of CO, CO_2, and H_2—known as syngas—on an industrial scale for a variety of processes, including methanol production. One of the basic challenges for the researchers in the Carbon2Chem project involves the treatment of smelter gas and the adaptation of the tried and tested processes to the syngas generated by steel production.

In a subproject of Carbon2Chem, Evonik is doing pioneering work to develop a new technology. The specialty chemicals company is developing catalysts that will be able to transform CO and H_2, which are essential components of smelter gas, into higher alcohols that could not have been produced by this method in the past (see the information box on page 41). In the future, the project team would ideally like to find ways to recover CO_2 directly.

Dr. Bernd Jaeger, who heads the catalyst research unit at Evonik, points out that this research is being driven by the impending transformation of the chemical industry. "The replacement of fossil sources of raw material with sustainable and CO_2-neutral input materials will transform the present-day material flows in our industry," he says. Higher alcohols could play a key role in this value chain. "However, we still don't have a cost-efficient and selective chemical production process for them," says Jaeger. This is where the Evonik researchers' idea comes into play: the design of customized catalysts that enable precisely this missing step toward a sustainable value chain by directly transforming smelter gases and carbon dioxide. →

From syngas to ethanol

A schematic diagram of the reaction processes



Catalysts reduce the amount of energy needed to trigger chemical reactions, thus accelerating them and making them more efficient. Sometimes they make a chemical reaction possible in the first place. And that's what is happening here. "Carbon dioxide and hydrogen molecules would never decide on their own to band together and form bigger molecules," says Dr. Dorit Wolf. "The catalyst gives them the help they need to take this step." Dr. Wolf, a chemist, is the head of Evonik's research department for process catalysts. From her base at the Hanau location, she coordinates the research cooperation between thyssenkrupp Industrial Solutions, Evonik, and research institutes for the Higher Alcohols project.

The team in Hanau has already produced a number of potential catalysts in recent years. The candidate catalysts, which consist of black powder, don't look very spectacular. This draws a visitor's attention all the more toward the container full of a violet substance that is standing under the laboratory's flue. "This is a cobalt salt we use as a raw material," explains Dr. Arne Reinsdorf, the head of development for mixed metal catalysts. And he reveals part of the secret behind all previous catalytic approaches: "There's always some combination of cobalt and copper, embedded in a carbon matrix in each case."

A MIX OF COPPER AND COBALT

In order to synthesize higher alcohols from a molecule such as CO, a catalyst must enable a series of very different reaction steps (see the infographic at left). To this end, the scientists need various active centers on the catalyst's surface. A homogeneous material consisting of a single substance would not be adequate, so the team is using a combination of cobalt and copper.

There are good reasons for this choice. The experts are relying on know-how that was gained previously from similar processes. Cobalt catalysts have proved their worth in the conversion of syngas into longer-chain hydrocarbons by means of the Fischer-Tropsch process.

Copper, in turn, is a tried and tested component of the production process for the simplest alcohol, methanol. "In the synthesis of higher alcohols we are trying to combine these two well-established processes in such a way that they initially form hydrocarbon chains that still contain the alcohol group OH at the end of the process," Reinsdorf says.

At the Evonik location in Hanau, laboratory assistant Mona Müller monitors the intermediate stage of a catalyst synthesis (left). The researchers use a rheometer to measure the flowability of their powders

The idea of using a combination of cobalt and copper was only the beginning of working out the details. These included questions regarding the optimal proportions of the two elements and the optimal chemical structures they should have for the process—for example, as metals or in an oxidized form, separated into individual particles or in a mixed phase. The researchers also knew that a trace amount of manganese would help to kick-start the catalyst, but they still had to find out whether it would be preferable to position it on top of, next to, or between the copper and cobalt particles.

They had already carried out numerous tests to determine the optimal proportion of manganese to use. This testing was supported by the Fraunhofer Institute for Environmental, Safety and Energy Technology (UMSICHT) in Oberhausen. That's where the catalyst samples from Hanau are being tested in a parallel reactor system made of stainless steel. Under precisely defined conditions of temperature and pressure, the experts are guiding syngas through the reactors and subsequently analyzing the results to find out what substances have been produced in what quantities.

Only the catalysts that have successfully passed the testing process at Fraunhofer UMSICHT will now be subjected to the next stage of testing in the project's second phase at thyssenkrupp in Duisburg. The technical center that was built there specifically for the Carbon2Chem project has a test setup that is similar to the first one but has three important differences: the reactors are bigger, the syngas supplied to them is extracted directly from the smelter gas of the neighboring steelworks, and the test series will run much longer so that the lifespan of the catalysts can be examined. →

Higher alcohols

Higher alcohols are defined as alcohols with more than one carbon atom. The simplest variant is ethanol, which is present in alcoholic beverages and is formed during the alcoholic fermentation process. Ethanol also plays a role in many chemical syntheses and as a fuel additive (E5, E10). Other higher alcohols serve, among other uses, as precursors in the production of active ingredients for pharmaceuticals and plant protection agents; surfactants for creams, salves, and cleaning agents; and solvents and plasticizers for plastics. Some alcohols are produced in volumes of several million tons per year.
Until now, some short-chain alcohols have been mainly produced via the fermentation of biomass, whereas the synthesis of longer-chain alcohols has been based on petroleum. In both cases, production using syngas (from waste) could be a sustainable alternative (see also the "People & Vision" section on page 9).

Although the starting materials and the interim steps of synthesis are still quite colorful, the finished catalyst material is always black

The results of the initial test series with more than 40 catalyst variants from Hanau were clear: It is definitely possible to use syngas to produce higher alcohols. This is a major success, but so far the process has generated too many unwanted byproducts—in particular, methane and short-chain alkanes. The newest generation of catalysts results in a more than 50 percent proportion of higher alcohols. "This means we've reached the target of the first project phase," says Wolf. But she's still not completely satisfied. "We need higher selectivity and even better yields," she adds.

INTEGRATION OF CARBON DIOXIDE

That's why the experts are continuing to work on optimizing the catalyst. The first test series showed them that a ratio of four parts of cobalt to one part of copper works well. Now they are specifically investigating process conditions such as the pressure, temperature, and retention time in the reactor. Other significant parameters could include the size of the metal crystallites and thus the incidence of crystal surfaces, corners, and edges in the powder. In order to gain a better understanding of these parameters with the help of experiments, the Evonik researchers are working together with experts from Ruhr-University Bochum and RWTH Aachen.

In parallel to this research, Dorit Wolf and Arne Reinsdorf are addressing another topic: also using carbon dioxide for the reaction. There was no carbon dioxide in the syngas that was used in the tests so far, but carbon dioxide is a major component of smelter gas. "We are now trying to design our catalyst in such a way that CO_2 can be integrated into the synthesis," says Wolf, adding that "this work is absolutely not trivial." If this effort succeeds, in the future it could also be possible to use other gas mixtures containing CO_2 as raw materials for the process.

But at the moment the researchers are focusing on increasing the catalyst's selectivity. They want to not only increase the yield of higher alcohols but also to more effectively control the length of the molecular chains that are produced. So far, the distribution of the chain lengths in the product mixes ranging from ethanol (with two C atoms) to hexanol (with six C atoms) has been sufficient. However, for later users of this technology it would be very useful to be able to precisely control the length of the chains. That's because, depending on the length of their molecular chains, various alcohols are of interest to very different market participants. Whereas the longer alcohols are especially in demand among producers of specialty chemicals, shorter alcohols such as ethanol and propanol could be used to produce synthetic fuels, and monomers could be used to make monomers for polyolefin production. Bernd Jaeger believes that there is great potential for a catalyst platform in this area. "Ideally, in the future we will offer a whole range of customized versions from which every user can choose the catalyst that matches his requirements," he says.

OTHER SOURCES OF RAW MATERIALS ARE POSSIBLE

Jaeger is also thinking one more step ahead. "Of course the ultimate goal must be to close material cycles," he says. And the process developed in the higher alcohols project could one day help to achieve exactly this goal. "We're developing a technology for the recovery of syngas, and this gas can also come from other sources," Jaeger adds. As soon as the process is established, biogas plants could also be considered as a source of raw material.

In the future, waste plastics could also supply the desired gas mixture if the plastics were decomposed at a high temperature and high pressure in the presence of small amounts of oxygen. Some companies are currently working to scale up this gasification process to the industrial level. "That would be interesting for processing waste flows that cannot be mechanically recycled, for example," says Jaeger, referring in particular to dirty or mixed waste that contains the plastics polyethylene or polypropylene. "These two polymers in particular are produced in large amounts, but to date they have seldom been chemically recycled," he says.

Both of these polymer types can in principle be produced from two higher alcohols: ethanol or propanol. In this process, the alcohols are initially converted into ethylene and propylene—substances that previously were extracted from petroleum. The individual building blocks ethylene and propylene could then be used to make new polymers—and thus new plastic products. A material cycle would be closed.

"We need higher selectivity and even better yields"

DORIT WOLF, HEAD OF THE RESEARCH DEPARTMENT FOR PROCESS CATALYSTS AT EVONIK

Carbon2Chem

Circulating carbon in a closed loop instead of emitting it into the environment—that is essentially the goal of the Carbon2Chem project. To reach this goal, the project aims to develop technologies that will make it possible to materially recover the smelter gas that is generated during steel production. Almost 20 partner companies from the chemical, energy, and steel sectors, including Evonik, as well as research institutes are devoting themselves to specific issues in a variety of subprojects. One of the areas being investigated is the use of smelter gas components to produce important chemicals such as ammonia, methanol, and higher alcohols. Another subproject is working to develop suitable processes for separating the substances contained in smelter gas.

The first phase of the project, from 2016 to 2020, had a budget of approximately €120 million, more than €60 million of which was provided by the German Federal Ministry of Education and Research (BMBF). The financial framework for the project's second phase, from 2020 to 2025, is even larger; it will be supported with up to €75 million by the BMBF.

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GEFÖRDERT VOM

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