Fuel for the energy revolution: plants such as this one belonging to Evonik in the town of Marl in North Rhine-Westphalia can generate hydrogen using surplus electricity from wind and solar plants. When combined with CO_2, hydrogen can generate synthetic fuels and raw materials such as methane for the chemical industry.

PHOTO: PICTURE ALLIANCE/SVENSIMON | MALTE OSSOWSKI

FROM POLLUTANT TO RAW MATERIAL

TEXT: KARL HÜBNER

Recycling efforts have focused primarily on paper, glass, and plastic. But CO_2 can be recycled, for example, into methane, the main ingredient in natural gas. A team at the Max Planck Institute for Dynamics of Complex Technical Systems in Magdeburg has developed a process which enables the methanation of CO_2 on an industrial scale. The process could help decrease the use of fossil raw materials.

It is one of the truly massive tasks connected with the energy revolution: the more progress we make in developing renewable energies, the more surplus green energy there will be at times when there is no immediate need to use it. Storing these surpluses is therefore crucial. Battery installations are one possible solution. Another possible approach, however, is to use the excess energy to synthesize chemical substances, which can then be used as energy sources or raw materials – a concept known as Power-to-X. Candidates include hydrogen, methanol, and ammonia.

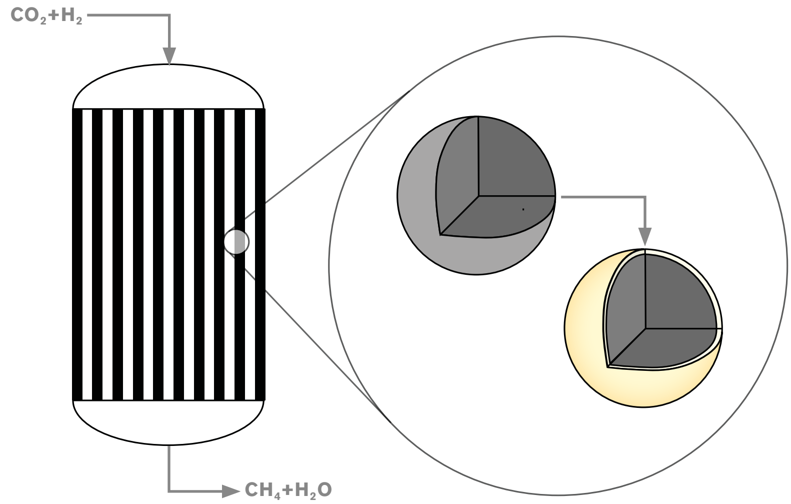
Another useful reservoir for green energy would be methane. As the main ingredient in natural gas, it could replace its fossil counterpart. A team led by Sundmacher the "methanation" of carbon dioxide (CO_2), in which hydrogen and CO_2 react with each other. The requisite hydrogen could be extracted by using the excess green electricity to electrolyze water. For CO_2, we could use industrial waste gas from cement, steel, and power plants, as well as from biogas plants. This would allow us to recycle greenhouse gas and limit further increases in CO_2 emissions. Methane created in this way could be used as an interim solution in gas power plants until they can be powered directly with hydrogen. "From our point of view, it would be especially useful to employ the methane as a raw material in the chemical industry, which could use it to make many products," says Kai Sundmacher, Director of the Process Engineering Department at the Max Planck Institute for Dynamics of Complex Technical Systems. "Unlike the energy industry, the chemical industry can't be completely decarbonized, because carbon is a crucial ingredient in most plastics, dyes, and medicinal substances, for example.

⟶

But like other industries, the chemical industry must defossilize its production processes by replacing them with climate-friendly alternatives."

A team led by Sundmacher has developed a process for CO_2 methanation that could be implemented on an industrial scale. After all, there are not yet any industrial plants for methanation that store renewable energy. This is partly due to technical challenges involving the chemical process. When CO_2 and hydrogen react, a lot of heat is released, which raises the temperature in the reactor. This temperature cannot be allowed to exceed 550 °C, however, because that would deactivate the nickel catalyst and quickly bring the reaction to a standstill.

As a result, there is a need for a design that keeps the reactor from getting too hot. Admittedly, there is a whole range of technical approaches, but many of them are expensive and therefore impractical. A process has yet to make it past the scale of a pilot plant. The team in Magdeburg has developed a concept that will yield economically viable quantities of methane, while preventing the temperature from getting too high. In the process, the researchers have taken the idea of core-shell catalyst pellets a step further. "This catalyst design, with a catalytically active core and an inactive shell, makes it possible to limit the reactor temperature, thus paving the way for industrial-scale methanation of carbon dioxide," Sundmacher explains.



GRAPHIC: GCO BASED ON WILEY-VCH PUBLISHER 2020

Protection from overheating: catalyst pellets consisting of an active core (gray) and an inactive shell (yellow) make it possible to control the reaction rate and hence the heat buildup. This is done by modifying the shell thickness and other properties. Consisting of bundles of pipes a few centimeters in diameter, the reactor is likewise designed in a way that prevents a sharp increase in temperature that could harm the catalyst.

The key: porosity and shell thickness

The key to the core-shell approach is the chemically inert, porous shell. Molecules intended to react with each other must first penetrate this shell to reach the catalytically active nickel sites on the core. It is only there that methane is formed. "The diffusion of the reactants through pores in the shells is what slows down the reaction rate, which in turn prevents the temperature from getting too high," explains Ronny Tobias Zimmermann, a chemical engineer on Sundmacher's team. What's more, by modifying the properties of the shell, such as its diameter or porosity, it is possible to determine how hot the reactor can get. "The thicker the shell, the lower the maximum possible temperature," explains Zimmermann. That's simply because a thicker shell increases the distance individual molecules have to travel on their way to the catalyst, thus slowing the reaction.

The Magdeburg team ran simulations and conducted subsequent experiments to determine the optimal properties and dimensions of both the core-shell catalyst pellets and the reactor. The resulting approach is to construct a reactor from a bundle of pipes three meters long and several centimeters thick, which are then filled with spherical core-shell catalyst pellets. Each pellet is around three millimeters in size, while the shell is only 0.1 millimeter thick,

SUMMARY

Carbon dioxide reacts with hydrogen to form methane, which could be used as a raw material for the chemical industry. Current process concepts cannot efficiently handle the heat generated by the reaction, which makes it difficult to implement CO_2 methanation on an industrial scale.

A team in Magdeburg has developed a new process based on core-shell catalyst pellets that enables precise control of the reactor temperature.

The Magdeburg process is load flexible, meaning that the supply of raw material can fluctuate. This is relevant from an industrial standpoint, because green hydrogen is not always available in the same quantity due to fluctuations in the supply of electricity from renewable sources.

roughly twice the thickness of a human hair. The methanation process involves running a mixture of hydrogen and carbon dioxide through pipes heated to around 300 °C. The resulting methane gas is collected at the other end of the pipes. Once purified, it can be fed into tanks or the natural gas network.

"Everything is designed to ensure that the reactor never gets hotter than 480 °C, regardless of how much starting material we put in," explains Zimmermann. The nickel cannot be deactivated, even when varying quantities of hydrogen and CO_2 are used. This flexibility and robustness are especially important when using renewable energies, whose electrical output fluctuates. The amount of hydrogen that is generated and that can react with the CO_2 fluctuates with the electricity supply. These fluctuations in reactant quantity are generally a major challenge for process engineering. Solutions that are good at handling fluctuations are called "load flexible." "Of course, it's possible to avoid the problem by storing the hydrogen temporarily and constantly retrieving it," says Sundmacher. "But that kind of storage is quite expensive." Consequently, there is a lot of interest in a load-flexible solution like the one just developed. As for where the reactors for methane extraction could be deployed, the Magdeburg team is focused mainly on places where surpluses in renewable energy can provide the necessary hydrogen, that is, wind farms and large solar plants.

Contact with chemical companies

In the meantime, the Magdeburg researchers have tested the core-shell concept for CO_2 methanation at the Institute's own pilot plant hall, which allows them to test processes under circumstances approximating industrial conditions. "We are now trying to introduce the process for industrial use, and are already in contact with chemical companies," says Sundmacher. But core-shell catalysts can be used for more than just synthesizing methane from carbon dioxide. They can also extract other substances of interest to the chemical industry, such as methanol, from the greenhouse gas. Generally speaking, the concept of tailor-made core-shell catalyst pellets can be applied to all gas phase reactions that generate a lot of heat, Sundmacher explains. That includes the production of ammonia from hydrogen and nitrogen. At present, the Institute in Magdeburg is also involved in a number of H2Mare projects, whose overall purpose is to use surplus electricity from offshore wind plants to generate hydrogen directly. Reactors with core-shell catalyst pellets for generating methane and ammonia are being tested as a way of possibly reusing the resulting hydrogen. Sundmacher and his team also see enormous potential in storing renewable electricity as chemicals and energy sources. He adds that the main limitation right now is the amount of renewable energy. But that should change in the future.

Pellets on trial: Ronny Tobias Zimmermann conducts experiments in which the different core-shell catalyst pellets are tested.

GLOSSARY

CO_2-METHANATION
is the conversion of carbon dioxide and hydrogen into methane.

DEFOSSILIZATION
refers to the movement away from fossil raw materials such as petroleum and natural gas towards renewable carbon-based raw materials such as biomass or CO_2.

DECARBONIZATION
means the abandonment of carbon-based energy sources, which release the greenhouse gas CO_2 when burned.

CORE-SHELL CATALYST PELLETS
is a chemical reaction accelerator consisting of an active core and a porous, inactive shell. The heat buildup in the reactor can be controlled by varying the thickness and porosity of the shell.