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Storage for Green Energy: Methanol - *Metha-Cycle* decouples wind power from electricity demand

Electrical energy from wind power is generated as spontaneously as the wind blows. But not always when it is needed. Therefore concepts for the turnaround in energy rely on hydrogen as an energy carrier, H_2, which can fire fuel cells and supply electricity when needed. Although H_2 can be easily produced in electrolysis using wind power, it is not easy enough to handle for further use, either as a gas or as a liquid. Chemists therefore suggest storing hydrogen in methanol. A research association under the leadership of LIKAT has shown for the first time how well this can be realized in practice. The project is called *Metha-Cycle* and was funded by the Federal Ministry of Economics (BMBF).

The concept allows companies and municipalities to be supplied with "green" electricity independent of wind power: wind turbines (optionally also photovoltaic systems) produce electrical energy, which is used to electrolytically produce hydrogen from water, which in turn is converted into methanol using CO_2.

Unlike hydrogen, methanol (the simplest representative in the group of alcohols) can be stored and transported easily - even over long distances. If required, it can be converted back into H_2 and used directly in a fuel cell to generate electricity. In the *Metha-Cycle* concept, the researchers also used the waste heat from the fuel cell to supply the catalyzed hydrogen release system with part of the necessary reaction heat.

"Such a direct coupling of regenerative energy, electrolysis and CO_2-based methanol synthesis as well as its reconversion via hydrogen to electrical energy has not yet existed," says project coordinator Dr. Henrik Junge from the Leibniz Institute for Catalysis in Rostock, LIKAT.

The Partners: Interdisciplinary Consortium

The test plant for hydrogen production from methanol was built by the project partner at the Friedrich-Alexander University (FAU) Erlangen-Nürnberg. In spring 2020 it demonstrated the functional efficiency of the concept with a running time of almost 500 hours. As part of the demonstrator, the fuel cell continuously produced electricity with an output of up to 39 Watts. It was developed by the Center for Fuel Cell Technology (ZBT) in Duisburg. The project partner at the FH Stralsund was responsible for the coupling of wind power, electrolysis and methanol synthesis.

The LIKAT developed the catalysts for the selective dehydrogenation of methanol at low temperatures - the heart of *Metha-Cycle*. The ATI Küste GmbH made calculations on the efficiency potential of the demonstrator.

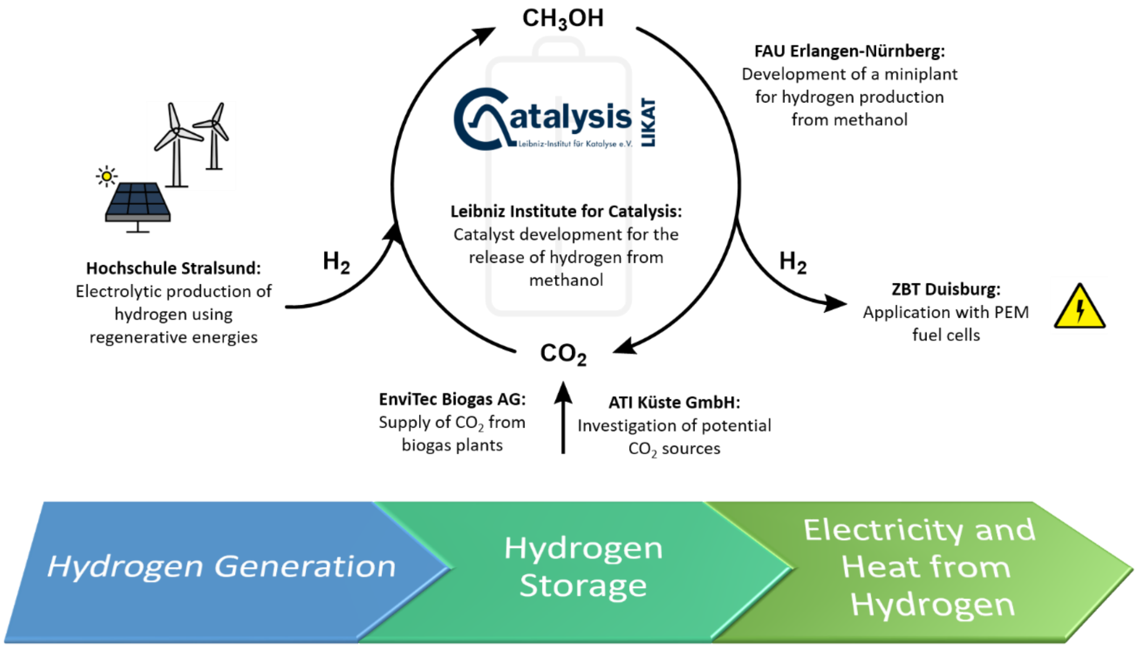

Fig. 1: Sector coupling in the Metha-Cycle project: An interdisciplinary consortium combines for the first time power generation from renewable energy, electrolysis, catalytized storage of hydrogen in methanol and subsequent release and conversion of the hydrogen into electricity in fuel cells.

LIKAT: Expertise on Hydrogen

LIKAT chemists have been researching on storing energy from renewable sources for a long time. At the beginning of the 2000s, they were the first laboratory to succeed in using formic acid as a hydrogen storage medium and to produce H_2 quasi at room temperature. Dr. Junge: "It was obvious to explore whether storing hydrogen in methanol was also possible." Indeed, methanol is even more effective than formic acid: it is able to chemically bind almost the threefold amount of hydrogen. But it usually requires high pressure and temperatures of several hundred degrees Celsius to release the hydrogen from methanol. This makes a general application less attractive.

In 2013 LIKAT chemists described in the magazine Nature how they produced H_2 and CO_2 from an aqueous methanol solution with the help of a ruthenium catalyst under mild conditions, below one hundred degrees Celsius. This reaction then had to be optimized. To permanently firing a fuel cell, for example, the process must provide sufficient H_2 per unit of time, and the gas must also have a certain purity.

The Way: „Mechanistic“ Analyses

For this purpose, the research group around Dr. Junge and LIKAT director Prof. Matthias Beller planned to analyse the molecular processes of the reaction. Henrik Junge has already been in discussion with partners for a joint project eligible for funding. Right from the beginning, the aim of the research was to "decouple the emergence of regenerative energy from its consumption", as he says. In the meantime, the whole world began to think about the role of hydrogen and methanol for an energy turnaround to save the climate. In autumn 2016, the BMWi finally took over the funding of *Metha-Cycle* for three and a half years with a total of 1.8 million euros.

The LIKAT researchers analyzed how the ruthenium catalyst works in the methanol solution to get H_2 and CO_2, thus releasing the hydrogen again. During these "mechanistic investigations" they discovered three cascade-like connected steps. At the end of each a part of the hydrogen and an additional substance is produced. This so-called intermediate is then further processed in the presence of the catalyst.

Dr. Junge: "The third step proved to be the slowest, it slowed down the whole system." In order to advance the cascade, the researchers decided on a bi-catalytic system: they gave their ruthenium catalyst a second catalyst as support. Surprisingly, they only needed to slightly modify their first catalyst.

Fig. 2: Mechanistic investigations take place on a laboratory scale; hydrogen release on immobilized catalyst in the reactor ..

Final Tuning in Erlangen

In Erlangen, the partners involved in the FAU's Department of Chemical Reaction Engineering (CRT) finally prepared the catalyst for a continuous process in a test plant. Within this test plant the research consortium ultimately proved the functionality of the concept. They impregnated a solid, highly porous carrier with the catalytically active complex from Rostock. Methanol and water vapor flow continuously over this carrier. The hydrogen produced is also continuously removed in order to be immediately converted into electricity in the connected fuel cell.

Literature:

C. H. Schwarz, A. Agapova, H. Junge, M. Haumann, *Catalysis Today* **2020**, *342*, 178-186; Immobilization of a selective Ru-pincer complex for low temperature methanol reforming – material and process improvements.