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Ready for Routine Operation

An X-ray photoelectron spectrometer called NAP-XPS analyzes the life cycle of catalysts at LIKAT.

They accelerate chemical processes without consuming themselves, is commonly said about catalysts. And yet their effect can diminish over time. What happens on their surface at the atomic level is being investigated by a state-of-the-art device in Rostock: the new X-ray photoelectron spectrometer (XPS) at the Leibniz Institute for Catalysis. It bombards atoms on the surface of a sample with X-rays and dislodges electrons. "From the energy required to do this, we can tell the character and state of the atom they came from," explains Dr. Stephan Bartling. He led the procurement of the NAP-XPS and prepared the device for routine operation.

New Possibilities for High-End Analytics

Conventional X-ray photoelectron spectrometers only work in an ultrahigh vacuum of 10^{-9} millibars, which is one millionth of normal atmospheric pressure. This is the only way to precisely determine the energy of the photoelectrons released by the X-ray beam, because they must not collide with other particles in the air on their way.

LIKAT has also been conducting research with such an XPS in a high vacuum. But that is not the usual reaction environment for catalysts. "For certain measurements, you simply need realistic analysis conditions," says Prof. Dr. Angelika Brückner, head of department “Catalytic in-situ-studies”. Analyses in the measuring chamber of the new instrument are carried out in the presence of (reactive) gases, hence the name NAP: **N**ear **A**mbient **P**ressure. In the future, this high-tech instrument will make it possible to analyze and optimize the function of catalysts in situ, i.e. under conditions close to the reaction.

1,1 Million Euros from EFRE Funds

Catalysis, as Angelika Brückner explains, is "in the broadest sense a surface phenomenon. A gas or liquid mixture flows along a porous, often metallic catalyst, for example. This surface contact alone ensures the desired reaction. The atoms on the surface of the catalyst play a role in this process and can sometimes lose their activity in the process, for example through irreversible changes in their oxidation state or through deposits.

Stephan Bartling: "By studying photoelectrons of the outer atomic layers of a material with the NAP-XPS, we can precisely see what happens to the atoms on the catalyst surface during a reaction." In a sense, the measurements can be used to map the life cycle of a catalyst.

While most NAP-XP spectrometers are installed at synchrotron sources and have limited availability, the new generation of these instruments can also be used in normal laboratory operation. In northern Germany, the NAP-XPS at LIKAT is the only laboratory instrument; nationwide, there are just under a dozen of these instruments available, and there are perhaps 60 machines in laboratory use worldwide. The Rostock acquisition received 1.1 million euros from the European Regional Development Fund (EFRE), which is primarily intended to expand interdisciplinary cooperation between science and business.

Abb. 1: Dr. Stephan Bartling prepares the new NAP-XPS for a measurement. (Picture: LIKAT/Nordlicht)

Oxidation of CO in Fuel Cells

One of the first requests for analysis concerned an area that is becoming increasingly popular both regionally and internationally: hydrogen technology, or more precisely, the service life and efficiency of fuel cells. Angelika Brückner explains the problem: hydrogen, the actual fuel for these cells, always contains traces of carbon monoxide, CO, due to the technology. But CO is poison for this technology; it damages the precious metal electrodes. "As chemists, we remove the CO by oxidizing it to CO_2. To do that, we use oxygen. And the hurdle is to prevent the oxygen from oxidizing the hydrogen at the same time." That's what the fuel cell needs as fuel, after all.

To solve the problem, laboratories around the world are experimenting with different catalysts. At LIKAT, one of the catalysts is a copper-containing catalyst based on cerium oxide, a rare-earth metal oxide known for its strong oxidizing power. Put simply, in this case the ceria donates the oxygen for the oxidation of CO, reducing it itself and making it inactive. To prevent this, it must at the same time recapture gaseous oxygen before it can tamper with the hydrogen.

This means the surface atoms of a good catalyst (in this case cerium) must change their oxidation state quickly and reversibly. "With our new device," says Dr. Bartling, "we were able to observe very nicely how this 'redox swing' works at different temperatures and gas compositions."

Literature

Elucidating the Nature of Active Sites and Fundamentals for their Creation in Zn-Containing ZrO2−Based Catalysts for Nonoxidative Propane Dehydrogenation

S. Han, D. Zhao, T. Otroshchenko, H. Lund, U. Bentrup, V. A. Kondratenko, N. Rockstroh, S. Bartling, D. E. Doronkin, J.-D. Grunwaldt, U. Rodemerck, D. Linke, M. Gao, G. Jiang, E. V. Kondratenko, *ACS Catal*. **2020**, *10*, 8933-8949. https://doi.org/10.1021/acscatal.0c01580

Further papers for publication of the new findings, including in NATURE CHEMISTRY, are in progress.

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