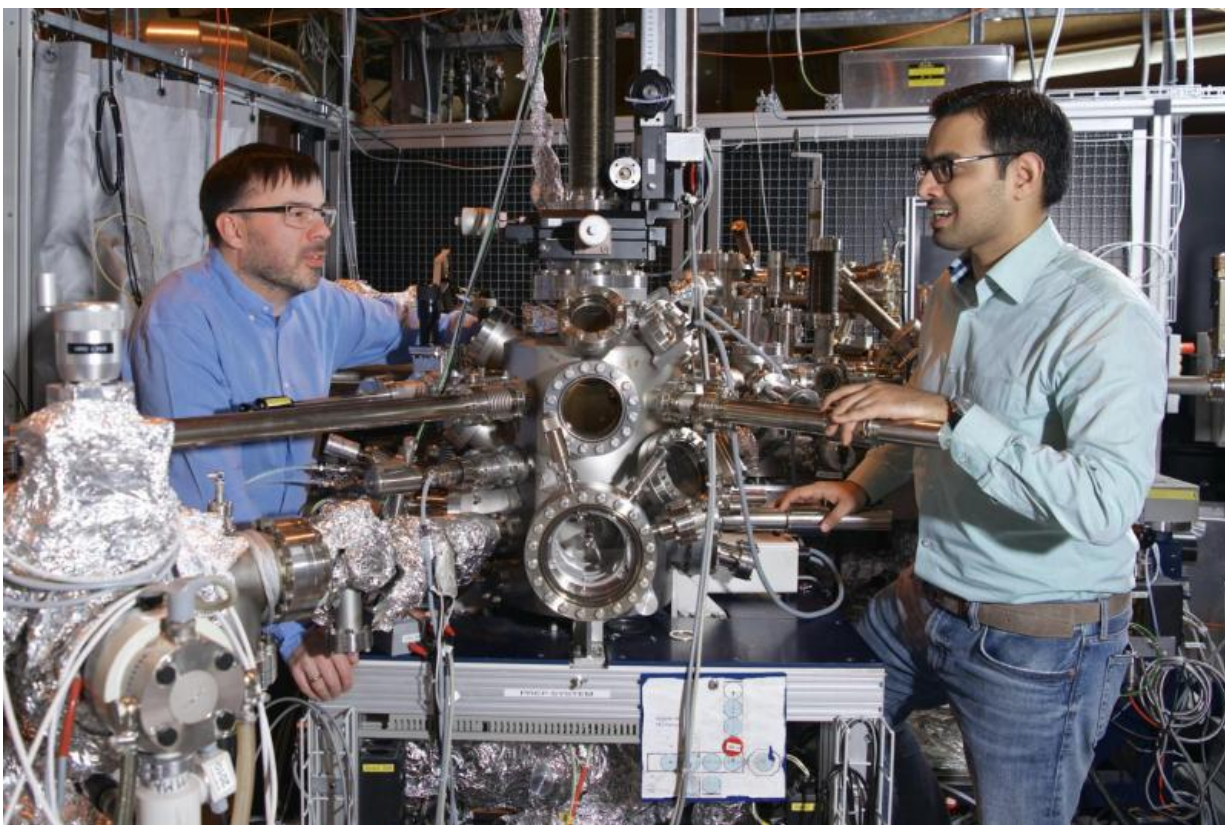


# Nanotechnology enables new insights into chemical reactions

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SIM beamline at the Synchrotron Light Source SLS of the Paul Scherrer Institute. The structures that allow for more precise studies of catalytic processes have been investigated here. Left: Armin Kleibert, beamline responsible, right: Waiz Karim, first author of the study published in the journal *Nature*. Credit: Paul Scherrer Institute/Markus Fischer

Eighty percent of all products of the chemical industry are manufactured with catalytic processes. Catalysis is also indispensable in energy conversion and treatment of exhaust gases. It is important for these processes to run as quickly and efficiently as possible; that protects the environment while also saving time and conserving resources. Industry is always testing new substances and arrangements that could lead to new and better catalytic processes. Researchers of the Paul Scherrer Institute PSI in Villigen and ETH Zurich have now developed a method for improving the precision of such experiments, which may speed up the search for optimal solutions. At the same time, their method has enabled them to settle a scientific controversy more than 50 years old. They describe their approach in the journal *Nature*.

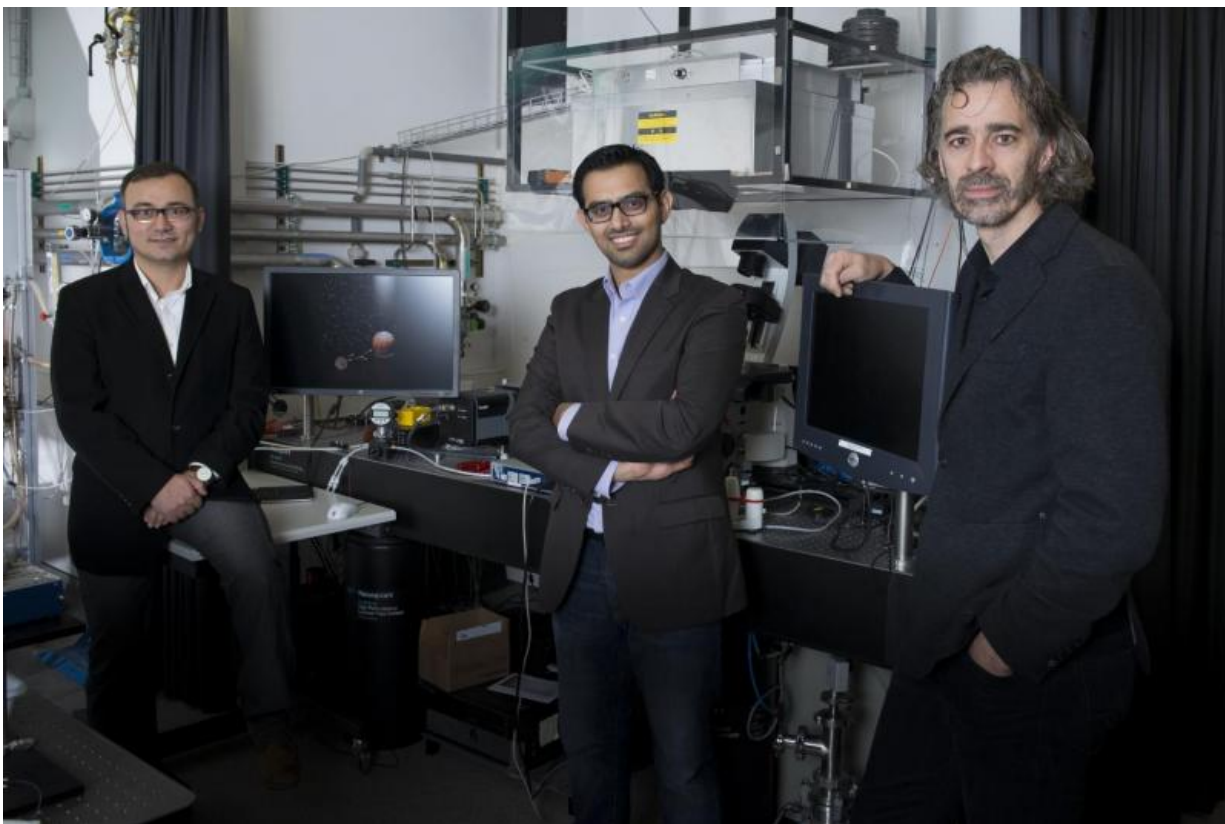
With a new process, Swiss scientists are making it easier for the chemical industry to investigate and optimise catalytic processes: "We have found a way to construct catalytic model systems - that is, experimental set-ups - accurate to one nanometre and then to track the chemical reactions of individual nanoparticles", says Waiz Karim, who is affiliated with both the Laboratory for Micro and Nanotechnology at the PSI and the Institute for Chemical and Bioengineering at ETH Zurich. "This makes it possible to selectively optimise the efficiency of catalytic processes."

Catalysis is a fundamental process in chemistry: Reactions of substances are triggered or accelerated through the presence of a catalyst. It plays a major role in the manufacture of synthetic materials, acids, and other chemical products, in the treatment of exhaust gases, and in energy storage (see Background). For this reason, the industry takes a great interest in optimising catalytic processes. "To do that, you need a deeper understanding of what is going on at the molecular level", says Jeroen van Bokhoven, head of the Laboratory for Catalysis and Sustainable Chemistry at the PSI and professor of Heterogeneous Catalysis at ETH Zurich, who led the study.

## Model experiment with unprecedented precision

This deeper understanding can be gained through the new approach: The researchers built a model system that enables them to study catalysis in the most minute detail. The experiments were carried out mainly at the PSI, and the theoretical basis was worked out at ETH Zurich. For the model experiment the team of Karim and van Bokhoven used [iron oxide](#), which was converted to iron through the addition of [hydrogen](#) and with assistance from the catalyst platinum. The platinum splits the molecular hydrogen ( $H_2$ ) into elemental hydrogen (H), which can more easily react with iron oxide.

The main attraction of their model: With state-of-the-art electron-beam lithography, otherwise used mainly in semiconductor technology, the researchers were able to place miniscule particles, consisting of just a few atoms each, on a support. The size of the iron oxide particles was only 60 nanometres, and the platinum particles were even smaller at 30 nanometres - about two-thousandths of the diameter of a human hair. The researchers positioned these particles in pairs on a grid-like model at 15 different distances from each other - in the first grid segment the platinum particle lay precisely on top of the iron oxide particle, and in the 15th segment, the particles lay 45 nanometres apart. In a 16th segment, the iron oxide was completely alone. "Thus we were able to test 16 different situations at once and control the size and spacing of the particles with one-nanometre accuracy", Karim explains. Then they vapourised the model with hydrogen and watched what happened.



Yasin Ekin, Waiz Karim and Jeroen van Bokhoven have developed a new more precise method for studying catalytic processes. Credit: Paul Scherrer Institute/Mahir Dzambegovic

For this observation in the molecular domain the team had, in an earlier project, employed a method called "single-particle spectromicroscopy" to analyse tiny particles by means of X-rays. The instruments needed to do this are available at the Swiss Light Source SLS of the PSI, a large-scale research facility that generates high-quality X-ray light. Not only is the precision of the particle positioning new, but the correspondingly accurate observation of chemical reactions - including simultaneous observation of many particles in different situations - had not been possible before: "In previous studies, placement of the nanoparticles of two different materials could be off by up to 30 nanometres", Karim



explains.

## **Distance-dependent spillover of hydrogen**

As it turned out, though, some chemical phenomena take place on an even smaller scale. One of these is the so-called hydrogen spillover effect, which the PSI and ETH researchers examined with their new model.

This effect contributes decisively to the efficiency of catalysis with hydrogen. It was discovered in 1964 but up to now could not be understood or visualised in detail. As a result, the circumstances under which it actually occurs remained controversial.

The team of Karim and van Bokhoven succeeded in analysing it for the first time with the precision needed: The hydrogen molecules split as soon as they encounter the platinum particle, and then the elemental hydrogen flows down the sides onto the support material. Then they spread out all around, the way water streams out of a spring. The hydrogen atoms meet the iron oxide particles and "reduce" them to iron, as researchers put it. "We were able to prove that how far the hydrogen flows depends on the support material", Karim reports. The farther it flows, the more the spillover can contribute to the catalysis. If the support consists of aluminium oxide, for example, which itself cannot be reduced, the hydrogen flows no farther than 15 nanometres. With reducible titanium oxide, in contrast, it flows over the whole surface. "Clearly, for some support materials it is important how tightly the particles sit on them."

## **Advancing chemical science**

Thus, with their new nanotechnology process, the PSI and ETH

researchers have clarified the circumstances of the hydrogen spillover effect. "Our method rests on three pillars", says Jeroen van Bokhoven, "the nanofabrication of the model system, the precise measurement of the [chemical reactions](#), and last but not least the theoretical modelling: In accordance with the experiments we were able to describe the process down to the molecular level." This, he suggests, could enable enormous advances in chemical science overall: "With this we are opening up a whole new dimension for the investigation and understanding of [catalytic processes](#). And with this understanding, industrial production processes can be optimised in a much more targeted way."

**More information:** Waiz Karim et al. Catalyst support effects on hydrogen spillover, *Nature* (2017). [DOI: 10.1038/nature20782](https://doi.org/10.1038/nature20782)

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