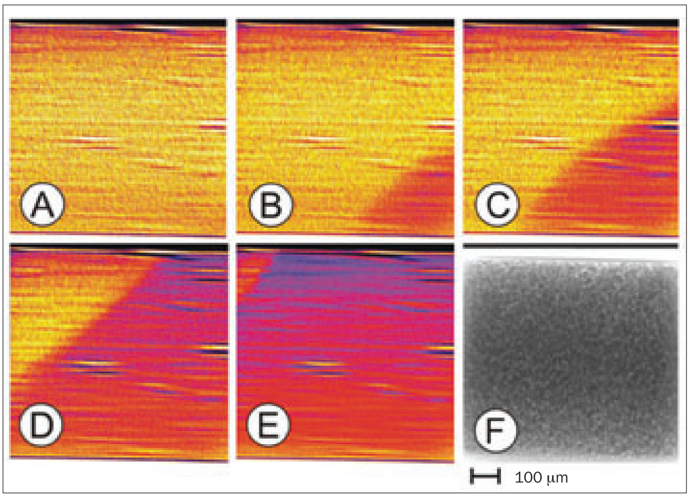
SCIENTISTS SHED LIGHT ON CATALYSIS MECHANISMS

Catalysis involves complex processes. Understanding catalysts on an atomic level should lead to an improvement in the performance of existing catalysts and help in the design of new ones. Thankfully, today's technology allows scientists to generate a much clearer picture of what happens during a catalytic reaction.



J-D Grunwalt (DTU) / C Schroer (TU Dresden) and Spotlight on Science

X-ray absorption through a catalyst bed during partial oxidation of methane. These images show the whiteline energy of Pt (Pt L3-edge; 11586 eV) as a function of time: (A) t1; (B) t1 + 1 s; (C) t1+ 2 s; (D) t1 + 5 s; (E) t1 + 33 s; (F) transmission image; (A) to (E) were obtained by subtraction of the X-ray absorption image at time t from (F), which was collected at t < t1 (t1 is the time of the last image where no gradient was found).

Synchrotron radiation makes it possible to carry out *in situ* experiments where scientists can monitor nanomaterials while the catalytic reaction takes place under realistic process conditions. It is not that simple, however, to recreate the real space and time conditions and at the same time monitor the structure and performance. This needs to combine physics, chemistry and reaction-engineering. Some teams, though, have taken on the challenge.

The partial oxidation of methane could be used for the production of hydrogen and synthesis gases (a mixture of CO and H_2). This is regarded as a first step in the so-called "gas-to-liquid technologies" to transform natural gas into liquid feedstocks, such as methanol. A change in a chemical reaction with time and space is often correlated to a variation in the state of the catalyst. Scientists therefore want to follow these changes in a spatiotemporal manner with a real catalyst to understand further what happens inside it.

Scientists from the Technical University of Denmark (DTU) and the Swiss Federal Institute of Technology in Zurich (ETH) specialise in monitoring reactions, such as the oxidation of methane. This is made possible by the X-rays of different synchrotron-radiation sources worldwide, the ESRF in particular.

2D monitoring of catalysts

"Only synchrotron sources provide the high intensity of X-rays needed for this kind of experiment. Hard X-rays have the excellent property of being able to penetrate materials, which allows us to engineer catalytic reactors that mimic the reactions under real conditions. This permits us to monitor the structure of the catalysts at the same time. That is also the reason why the excellent staff at the synchrotron sources make the effort to build up our catalytic reactors directly at the beamlines, although we could run them more easily directly in our own laboratory, but without looking into the reactor," explains Jan-Dierk Grunwaldt, the professor leading the team that has recently moved from ETH Zurich to the Department of Chemical and Biochemical Engineering at DTU.

One of the latest achievements by the group is the insight into the change in structure of palladium catalysts while the methane is oxidising. This was obtained using a flame-made catalyst that underwent a reduction and sintering of palladium particles during the oxidation of methane at more than 750 °C. Scientists noticed that this led to reduced catalytic activity by using X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD) and online catalytic data at the Swiss-Norwegian beamline at the ESRF. This was the first time that the three techniques were used simultaneously at such high temperatures, and the results revealed a direct correlation between the structure of the catalyst and its performance.

The team, in collaboration with a group from the Technical University Dresden, Germany, also studied the structural changes of rhodium particles on ignition of the aforementioned catalytic partial oxidation of methane. On this occasion, the scientists used a spectroscopic cell with a gas supply and a CCD camera, and they combined X-ray absorption spectroscopy and online mass spectrometry at ID26. Thanks to these novel techniques, scientists were able to carry out spatially resolved 2D monitoring of the catalyst inside the catalyst bed (figure 1). They observed strong changes in the structure once the catalytic reaction was taking place along the catalyst bed. This became a Spotlight on Science (number 46) on the ESRF website.

These technical developments have also allowed the team to investigate the formation of nanomaterials together with Greta Patzke of the University of Zurich, such as tungsten/molybdenum oxides with a hexagonal tungsten bronze structure. These oxides belong to the family of transition metal oxides, which are interesting for selective oxidation reactions. The scientists could observe their transformation into other mixed nanostructures only at temperatures of more than 300 °C in atmospheres containing oxygen and hydrogen. The use of XAS and XRD at the Swiss-Norwegian beamline provided complementary information about the change in structure in short- and long-range order. By using additives during hydrothermal synthesis, the researchers could observe how the oxides formed and changed morphology.

The team now faces the challenge of combining XRD and XAS with Raman spectroscopy, which recently became possible at the Swiss–Norwegian beamline. "The first experiments seem very interesting. Apart from the possibility to study further important reactions, the spatiotemporal development of catalysts and tomographic studies are especially fascinating," explains Grunwaldt. •

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References

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