The structure of a working catalyst ; from flat surfaces to nanoparticles

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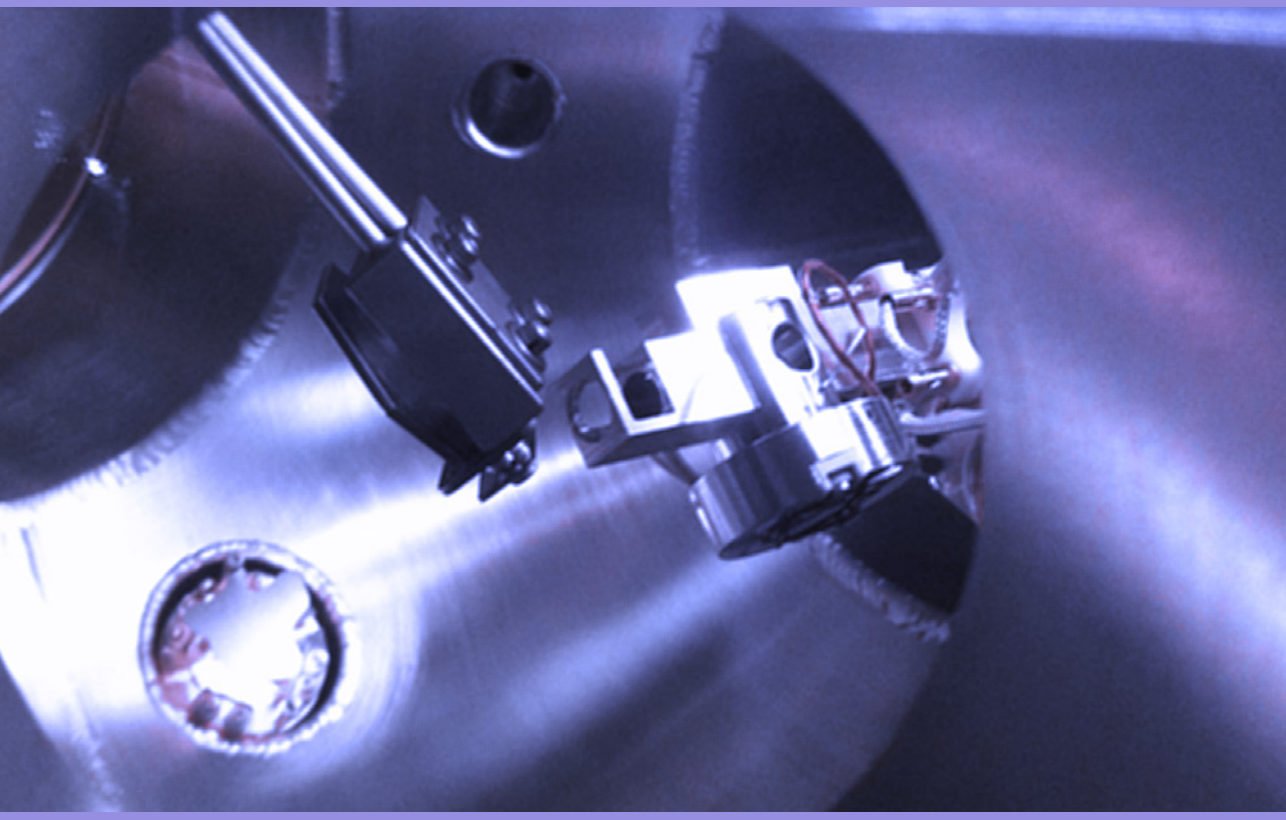
In memory of my grandfather, dr. Kees Kruit.



About this thesis

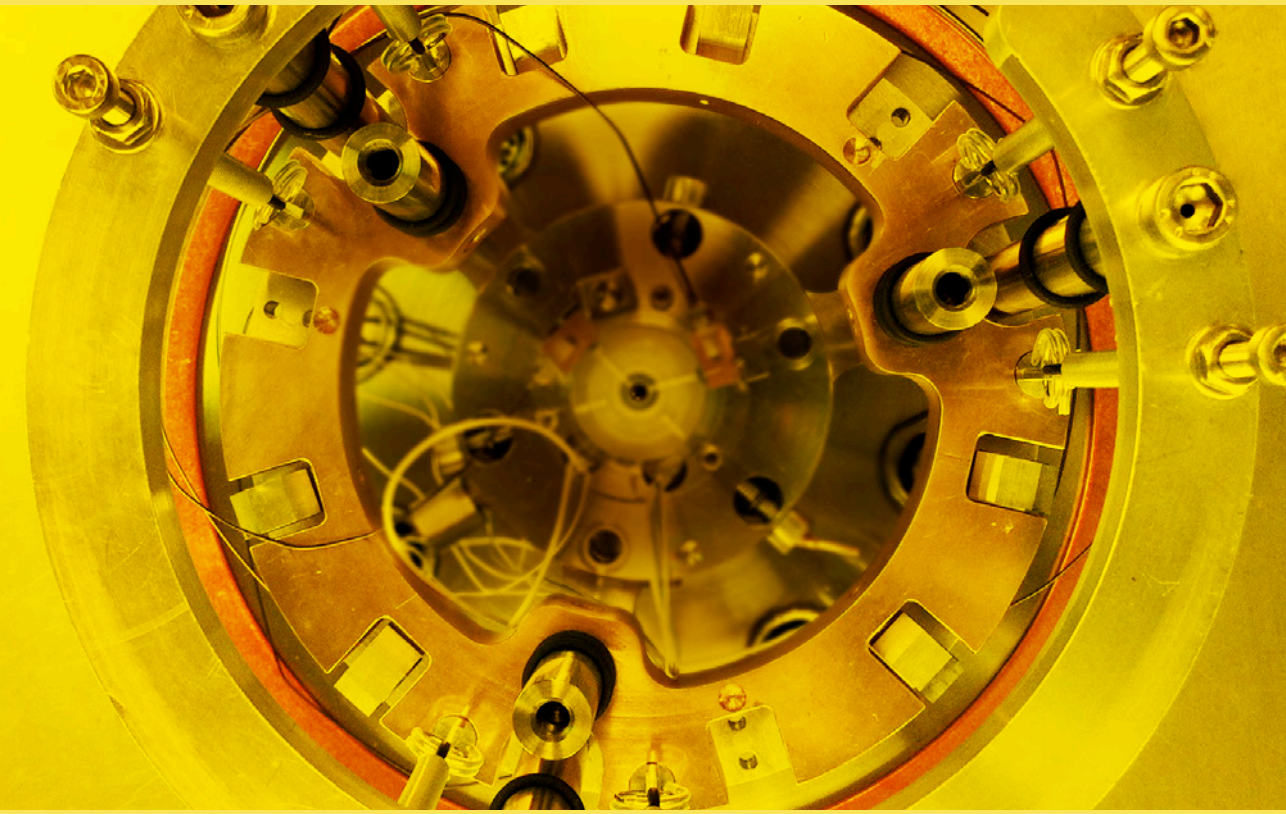
Catalysis is the working horse of the chemical industry. In many cases, it is a poorly understood process that takes place at the surfaces of nanoparticles under relatively harsh conditions, such as high pressures and high temperatures.

This thesis focuses on new approaches to acquire atomic-scale information on catalytic processes on metal nanoparticles in high-pressure, high-temperature conditions. This thesis starts with a general introduction that motivates the need for *operando* or *in-situ* observations and advocates the simultaneous use of a combination of atomic-scale measurement techniques. The body of this thesis is organised in two parts that can be read independently.

Part I takes a comprehensive approach to the development of novel instruments and methods for *in-situ* experiments on model catalysts under working conditions. It introduces the mechanical and electronic hardware of the ReactorAFM, the world's first high-pressure, high-temperature non-contact Atomic Force Microscope. In addition, it describes two software packages for the analysis of *in-situ* microscopy data, and for the analysis of surface X-ray diffraction data.

In part II we have applied our new instrument in combination with other, recently developed *in-situ* measurement techniques to study catalytic model systems at atmospheric pressures and elevated temperatures. We first describe a study of the interaction of gas mixtures of nitric oxide and hydrogen on the Pt(110) surface, using surface X-ray diffraction. This study serves as a stepping stone for the next chapter, where we exposed a Pt nanoparticle model catalyst to mixtures of nitric oxide and hydrogen in a high-pressure reaction cell in a transmission electron microscope. Finally, we have investigated spontaneous reaction oscillations on Pd nanoparticles during the catalytic oxidation of carbon monoxide. Using a combination of four *in-situ* techniques, including our new ReactorAFM, we have established the periodic formation and reduction of a thin oxide shell on the nanoparticles during the oscillations.

As will be explained in the first chapter, the differences between the idealised world of traditional surface science and the complex world of practical catalysis are commonly categorised into the *pressure gap* and the *materials gap*. The approach taken in this thesis to combine several *in-situ* measurement techniques, is necessary to bridge the *pressure gap* and at the same time take a significant step across the *materials gap*.



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