Transmission electron microscopy on live catalysts

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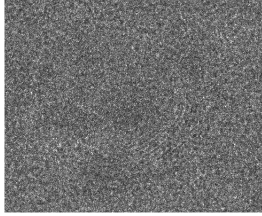


About the illustrations in this thesis

In order to provide an impression of the laboratory, the instruments and the experimental geometries that have contributed to this PhD thesis, I have provided several photographs and other illustrations.

The cover of this thesis is an artist's impression of the inside of a nanoreactor channel (rendered by Merijn Pen). It features catalyst nanoparticles that cover the channel surface and gas molecules that are flowing over them.

The small illustrations on the top right corner of each page combine into a flip book. Quickly flick all pages from front to back to watch an *in situ* movie of a cobalt nanoparticle that gets covered progressively with layers of carbon atoms. The movie is described and analyzed in detail in Chapter 5.

The first page of each chapter is accompanied by an illustration, in most cases directly related to that chapter. Chapter 1 shows a Philips CM30T microscope, the oldest operational transmission electron microscope in the HREM group at the Delft University of Technology. Installed in 1989, it is now often used for student TEM training. After sufficient training, access is provided to more sophisticated TEMs. The newest electron microscope is the FEI Titan^3, shown at the start of Chapter 4.

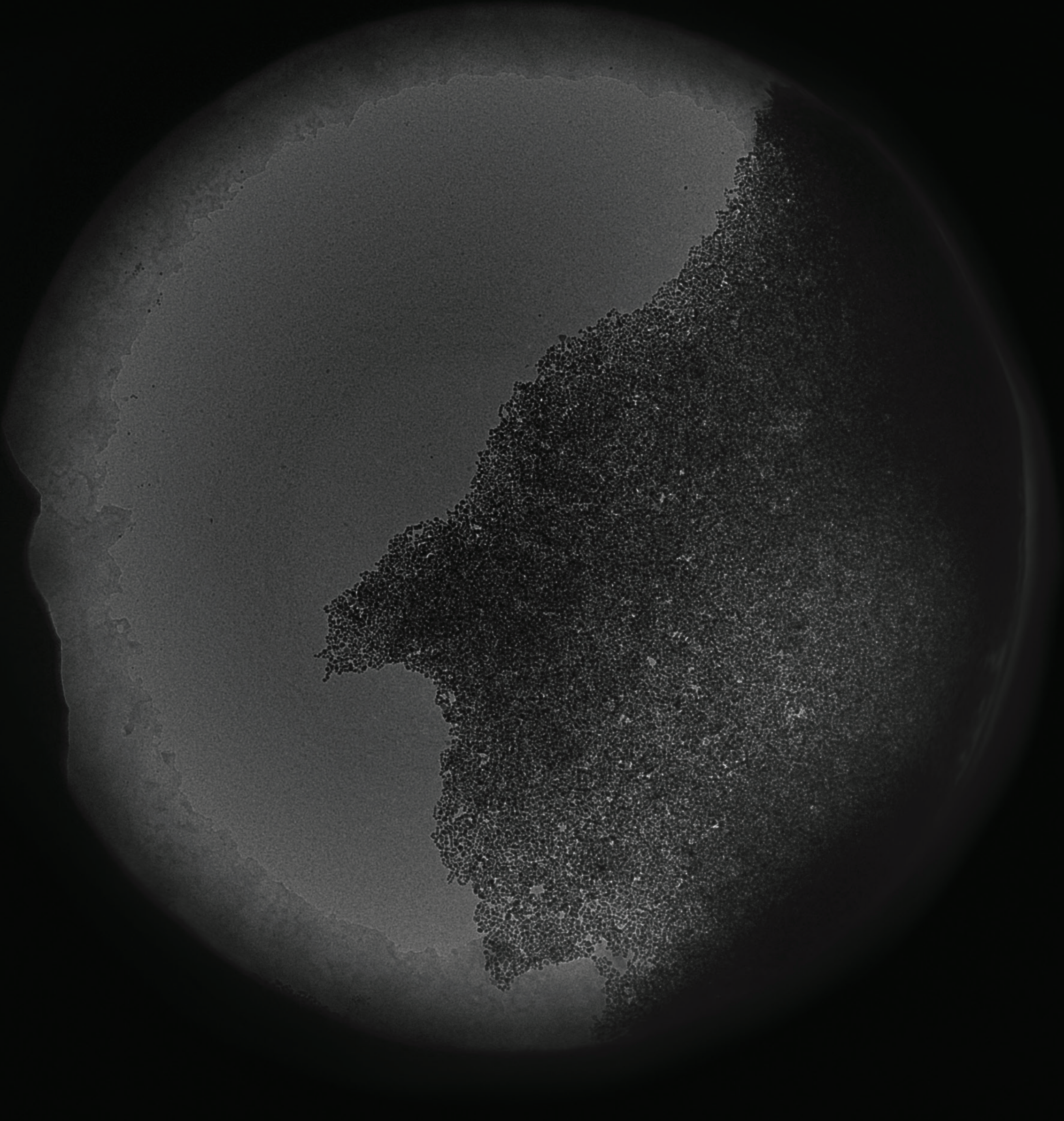
The grayscale image next to the Table of Contents displays a TEM image of a sample grid. The small dark lumps are pieces of γ-Al_2O_3 support material, carrying MoS_2-slabs. The start of Chapter 2 shows a high-magnification TEM image of such a particle supporting MoS_2-slabs. A STEM-HAADF image of CoRe nanoparticles on an ultrathin carbon sample grid is shown next to the Curriculum Vitae of the author.

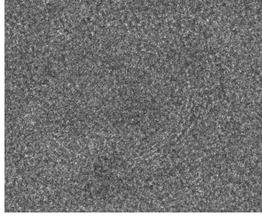
The *in situ* TEM sample holder is shown at the start of Chapter 5, the tip of the holder opened, revealing a loaded nanoreactor.

During sample loading, we monitor the liquid flowing through the nanoreactor by use of an optical microscope. This is shown by the photograph accompanying the Dutch Samenvatting. Notice that the central channel is partially filled with liquid, which is visible at the top left and in the entire right side of the channel. A set of nanoreactors in a gel box is shown at the Summary chapter.

A low-magnification TEM image of a nanoreactor, showing the 41 electron-transparent windows, each window 7 μm in diameter, is placed to the left of this text. After loading nanoparticles into the nanoreactor, the windows get covered with nanoparticles, as is shown at the Acknowledgements section.

Photographs of the gas flow system are provided at the start of Chapter 3 and next to the List of Publications.





Acknowledgements

The work described in this thesis is the result of many people working together rather than that of solely my own efforts. I would like to express my gratitude to the people that contributed to this work or supported me in any other way during my time as a PhD student.

Firstly, I would like to thank my promotor Joost Frenken and co-promotor Patricia Kooyman for giving me the opportunity to start this endeavor, sharing their scientific guidance, passion and inspiration, and for the many hours Patricia spent with me at the TEM. I am grateful to Ellie van Rijsewijk for all her administrative help and support. My work at TU Delft was made possible by Henny Zandbergen, who provided access to the TEM facilities, and by the support of Marijke van der Veen. Frans Tichelaar taught me all the details about TEM experiments and was essential in my work at the TEMs. Laboratory work was made possible by Johan Bakker (Leiden University), Tom de Kruijff and Jouk Jansen (TU Delft), and by support from the Fine Mechanical Department of Leiden University by Mirthe Bergman. Irene Groot was of great help by directing our group in Leiden during the last three years.

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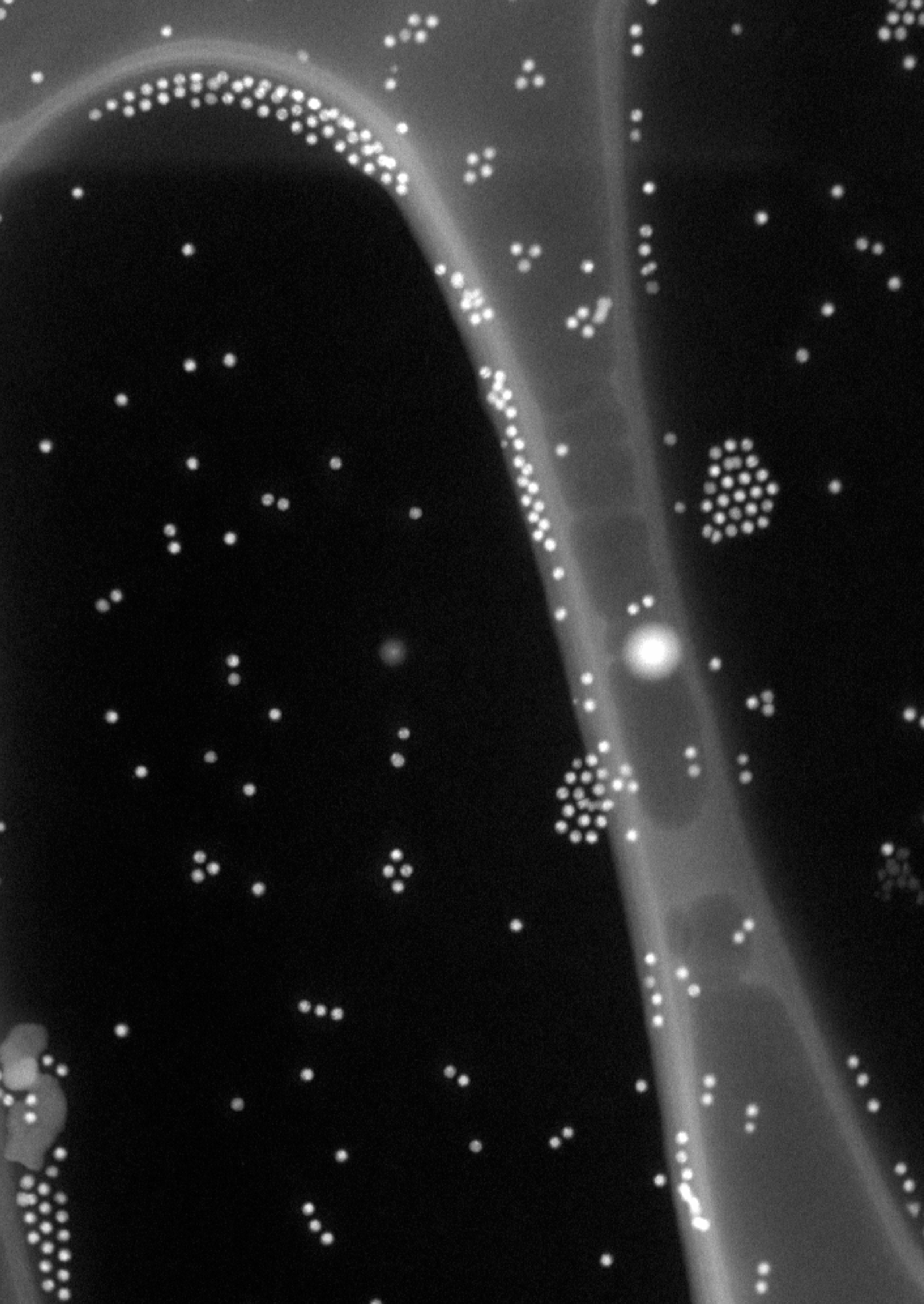
The *in situ* TEM experiments were made possible by the supply of nanoreactors via Fredrik Creemer, Bruno Morana, and Gregory Pandraud (Else Kooi Lab); and the support of Pleun Dona, Bas Hendriksen, and Luigi Mele (FEI).

The various catalysts used during my experiments were kindly provided via the pleasant collaborations we had, with Anja Sjåstad and Eirini Zacharaki (University of Oslo), and with the experimental support via Lennart van Haandel, Emiel Hensen, and Miao Yu (TU Eindhoven).



Curriculum Vitae

Marien Bremmer was born on April 9, 1990 in Katwijk, the Netherlands. He got his highschool degree from the Visser 't Hooft Lyceum in Leiden in 2008. Bremmer continued his studies through a BSc in Molecular Science and Technology (MST) at Leiden University and Delft University of Technology, obtaining his degree in 2011 after a research project on the synthesis of coiled-coil peptides and their applications in lipid membrane vesicle fusion, in the research group of Prof. Dr. Alexander Kros. During his MSc project in Chemistry at Leiden University, he continued his research on lipid membrane layers in the group of Kros. Using liquid-cell ellipsometry and liquid-cell AFM he studied the properties of multilayer self-assembled lipid layers, supported on silicon wafers. Before graduating, he finished a second research project at Leiden Probe Microscopy BV, where he built and used a tabletop gas flow reactor for catalysis experiments. Using the reflection of visible light, he studied the effect of CO oxidation conditions on the surface of a Pd single crystal.

Under the supervision of Prof. Dr. Joost Frenken and Prof. Dr. Patricia Kooyman he went on to pursue a PhD at the Huygens-Kamerlingh Onnes Laboratory of Leiden University, in collaboration with the Zandbergen Lab at Delft University of Technology. He studied (Ni/Co)MoS_2 catalyst particles in collaboration with Prof. Dr. Emiel Hensen from Eindhoven University of Technology, using quasi *in situ* transmission electron microscopy. In collaboration with Prof. Dr. Anja Sjåstad from University of Oslo he performed *in situ* TEM experiments on cobalt nanoparticles using gas flow systems, a dedicated *in situ* TEM sample holder, and nanoreactors to contain catalyst samples.

List of Publications

Bremmer, G.M.; van Haandel, L.; Hensen, E.J.M.; Frenken, J.W.M.; Kooyman, P.J.
Instability of $NiMoS_2$ and $CoMoS_2$ hydrodesulfurization catalysts at ambient conditions: a quasi *in situ* high-resolution transmission electron microscopy and x-ray photoelectron spectroscopy study.
Journal of Physical Chemistry C, **2016**, *120* (34), 19204–19211; DOI: 10.1021/acs.jpcc.6b06030. (Chapter 2 of this thesis)

Bremmer, G.M.; van Haandel, L.; Hensen, E.J.M.; Frenken, J.W.M.; Kooyman, P.J.
The effect of oxidation and resulfidation on (Ni/Co)MoS_2 hydrodesulfurization catalysts.
In preparation (Chapter 3 of this thesis)

Zacharaki, E.; Bremmer, G.M.; Kalyva, M.; Kooyman, P.J.; Fjellvåg, H.; Sjåstad, A.O.
Cobalt-rhenium β-Mn type bimetallic nanoparticles prepared via colloidal chemistry.
Submitted (Chapter 4 of this thesis)

Bremmer, G.M.; Zacharaki, E.; Sjåstad, A.O.; Navarro, V.; Frenken, J.W.M.; Kooyman, P.J.
In situ TEM observation of the Boudouard reaction: Multi-layered graphene formation from Co on cobalt nanoparticles at atmospheric pressure.
Faraday Discussions, **2017**, *197*, 337–351; DOI: 10.1039/C6FD00185H. (Chapter 5 of this thesis)

Bremmer, G.M.; Zacharaki, E.; Sjåstad, A.O.; Navarro, V.; Frenken, J.W.M.; Kooyman, P.J.
In situ TEM observation of multilayer graphene formation from Co on cobalt nanoparticles at atmospheric pressure.
Microscopy and Microanalysis, **2017**, *23*, 896–897; DOI: 10.1017/S1431927617005141

Bremmer, G.M.; van Haandel, L.; Hensen, E.J.M.; Frenken, J.W.M.; Kooyman, P.J.
A quasi *in situ* HRTEM study of the air stability of (Ni/Co)MoS_2 hydrodesulfurization catalysts.
Microscopy and Microanalysis, **2015**, *21* (S3), 801-802; DOI: 10.1017/S1431927615004808

van Haandel, L.; Longo, A.; Bremmer, G.M.; Kooyman, P.J.; Bras, W.; Hensen, E.J.M.; Weber, Th.
Formation of supported molybdenum disulfide nanoparticles under industrial conditions.
In preparation

van Haandel, L.; Bremmer, G.M.; Hensen, E.J.M.; Weber Th.
The effect of organic additives and phosphoric acid on sulfidation and activity of (Co)Mo/Al_2O_3 hydrodesulfurization catalysts.
Journal of Catalysis, **2017**, *351*, 95–106; DOI: 10.1016/j.jcat.2017.04.012

van Haandel, L.; Bremmer, G.M.; Hensen, E.J.M.; Weber Th.
Influence of sulfiding agent and pressure on structure and performance of CoMo/Al_2O_3 hydrodesulfurization catalysts.
Journal of Catalysis, **2016**, *342* (C), 27–39; DOI: 10.1016/j.jcat.2016.07.009

van Haandel, L.; Bremmer, G.M.; Kooyman, P.J.; van Veen, J.A.R.; Weber, Th.; Hensen, E.J.M.
Structure-activity correlations in hydrodesulfurization reactions over Ni-promoted $Mo_xW_{(1-x)}S_2/Al_2O_3$ catalysts.
ACS Catalysis, **2015**, *5* (12), 7276–7287; DOI: 10.1021/acscatal.5b01806

Onderwaater, W.; Taranovskyy, A.; Bremmer, G.M.; van Baarle, G.; Frenken, J.W.M.; Groot, I.M.N.
From dull to shiny: A novel setup for reflectance difference analysis under catalytic conditions.
Review of Scientific Instruments, **2017**, *88*, 023704; DOI: 10.1063/1.4975930

Versluis, F.; Voskuhl, J.; van Kolck, B.; Zope, H.; Bremmer, G.M.; Albregtse, T.; Kros, A.
In situ modification of plain liposomes with lipidated coiled coil forming peptides induces membrane fusion.
Journal of the American Chemical Society, **2013**, *135* (21), 8057-8062; DOI: 10.1021/ja4031227