



Universiteit
Leiden
The Netherlands

ReactorSTM : imaging catalysts under realistic conditions

Herbschleb, C.T.

Citation

Herbschleb, C. T. (2011, May 10). *ReactorSTM : imaging catalysts under realistic conditions*. *Casimir PhD Series*. Retrieved from <https://hdl.handle.net/1887/17620>

Version: Not Applicable (or Unknown)

License: [Leiden University Non-exclusive license](#)

Downloaded from: <https://hdl.handle.net/1887/17620>

Note: To cite this publication please use the final published version (if applicable).

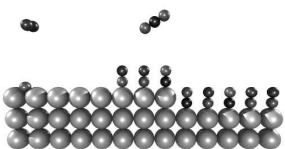
List of publications

1. *Catalytic activity of the Rh surface oxide: CO oxidation over Rh(111) under realistic conditions*; J. Gustafson, R. Westerström, O. Balmes, A. Resta, R. van Rijn, X. Torrelles, **C. T. Herbschleb**, J. W. M. Frenken, and E. Lundgren; *J. Phys. Chem. C* **114**, 4580 (2010).
2. *Reply to “comment on ‘Catalytic activity of the Rh Surface Oxide: CO Oxidation over Rh(111) under realistic conditions’ ”*; J. Gustafson, R. Westerström, O. Balmes, A. Resta, R. van Rijn, X. Torrelles, **C. T. Herbschleb**, J. W. M. Frenken, and E. Lundgren; *J. Phys. Chem. C* **114**, 22372 (2010).
3. *High-pressure STM study of NO reduction by CO on Pt(100)*; **C.T. Herbschleb**, S.C. Bobaru, and J.W.M. Frenken; *Catalysis Today* **154**, 61 (2010).
4. *High-Pressure STM for studying catalysis under industrial conditions*; **C.T. Herbschleb**, P.C. van der Tuijn, Q. Liu, G. Verdoes, M.E. Cañas-Ventura, L. Crama, D. Stoltz, J.W. Bakker, V. Navarro-Paredes, I. Taminiau, G.J.C. van Baarle, A. Ofitserov, M. Bergman, and J.W.M. Frenken; in preparation for submission to *Rev. Sci. Instr.*
5. *ReactorAFM; Ultrahigh vacuum/high-pressure flow reactor for atomic force microscopy studies close to conditions for industrial catalysis*; M. E. Cañas-Ventura, S. Roobol, W. Onderwaater, P.C. van der Tuijn, **C.T. Herbschleb**, Q. Liu, G. Verdoes, R. Koehler, D. Stoltz, J.W. Bakker, G.J.C. van Baarle, A. Ofitserov, V. Navarro-Paredes, I. Taminiau, M. Bergman, and J. W. M. Frenken; in preparation for submission to *Rev. Sci. Instr.*
6. *High-pressure STM study of hydro-desulphurization of thiophene on MoS₂/Au(111)*; **C.T. Herbschleb**, Q. Liu, J.W. Bakker, B.J. Nelissen, S. Helveg, and J.W.M. Frenken; in preparation.
7. *Oxide versus Metal – Direct STM imaging of the surface oxide on Pt(110) during CO oxidation at atmospheric pressures*; **C.T. Herbschleb**, Q. Liu, V. Navarro-Paredes, J.W. Bakker, M.E. Cañas-Ventura, D. Stoltz, and J.W.M. Frenken; in preparation.



Curriculum Vitae

Cornelis Thaddeus Herbschleb is geboren op 1 november 1983 te Leeuwarden. Na het behalen van zijn gymnasium-diploma in juni 2001 begon hij zijn studie natuurkunde aan de Universiteit van Leiden, waar hij in juni 2006 zijn doctoraal diploma behaalde. Zijn eerste onderzoeksstage bestond aan de ene kant uit het construeren, plaatsen en beheren van kosmische stralingsdetecoren in Leiden en omgeving (alsmede in Khartoum) onder begeleiding van prof. dr. Pierre van Baal. Dit werk vond plaats in nauw contact met het Nederlands Instituut voor Kern en Hoge Energie Fysica. Aan de andere kant heeft hij tijdens deze onderzoeksstage een dergelijke stralingsdetector geïntegreerd met MiniGRAIL (Mini-Gravitational Radiation Antenna In Leiden) in de groep van prof. dr. Giorgio Frossati. De tweede onderzoeksstage vond plaats in de Interface Physics groep onder begeleiding van prof. dr. Joost Frenken en had betrekking op het onderzoek van de werking van katalysatoren met behulp van een hoge-druk STM. Hij vervolgde het werk aan deze opstelling tijdens zijn promotie, in dienst van de Interface Physics groep, verbonden aan de Universiteit Leiden. Hij heeft tijdens zijn promotie ook gewerkt aan de ontwikkeling van een nieuwe, sterk verbeterde versie van de ReactorSTM, waarin resolutie, robuustheid, drukbereik en gebruikersgemak een grote rol hebben gespeeld. Alsmede heeft hij de eerste succesvolle metingen met deze apparatuur verricht. Tijdens zijn promotie heeft hij deel uitgemaakt van NanoNed (www.nanoned.nl) en het SmartMix programma NIMIC (www.realnano.nl). Daarnaast is hij project coördinator geweest van EuroPhysicsFun, een Europees platform voor natuurkundeshows in Europa dat ondermeer jaarlijks het congres “Show Physics” organiseert.

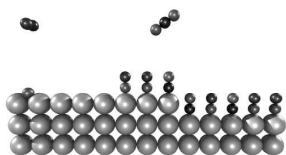


Bibliography

- [1] J.J. Berzelius; Edinburgh New Philosophical Journal **21**, 223 (1836)
- [2] Heterogeneous catalysis in industrial practice, 2nd ed.; C.N. Satterfield; McGraw-Hill, New York (1991)
- [3] Encyclopedia of chemical technology volume 1, 3rd ed.; H.F. Mark et al.; John Wiley & Sons (1978)
- [4] [http://nobelprize.org/nobel_prizes/chemistry/laureates /2007/](http://nobelprize.org/nobel_prizes/chemistry/laureates/2007/)
- [5] The Basis and Applications of heterogeneous catalysis; M. Bowker; Oxford Chemistry Primers (1998)
- [6] Introduction to Surface Chemistry and Catalysis; G.A. Somorjai; Wiley, New York (1993)
- [7] Otto Roelen, pioneer in industrial homogeneous catalysis; B. Cornils et al.; Angewandte Chemie International Edition **33**, 2144 (1994)
- [8] [http://www.chemguide.co.uk/physical/catalysis/ introduction.html](http://www.chemguide.co.uk/physical/catalysis/introduction.html)
- [9] Automobiles and pollution; P. Degobert; Éditions Technip. (1992)
- [10] Surface studies by scanning tunneling microscopy; G. Binnig et al.; Phys. Rev. Lett. **49**, 57 (1982)
- [11] Introduction to scanning tunneling microscopy; C. Chen; Oxford series in optical and imaging sciences (1993)
- [12] Atomic-scale study of a hydrodesulfurization model catalyst; J.V. Lauritsen; PhD thesis, University of Århus (2002)
- [13] Scanning tunneling microscopy; J.A. Stroscio and W. Kaiser; Academic Press, San Diego (1993)



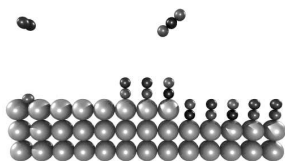
- [14] Growth mechanisms of epitaxial metallic oxide SrRuO₃ thin films studied by scanning tunneling microscopy; R.A. Rao et al.; Appl. Phys. Lett **71**, 1171 (1997)
- [15] Epitaxial growth of thin magnetic cobalt films on Au(111) studied by scanning tunneling microscopy; B. Voigtländer et al.; Phys. Rev. B **44**, 10354 (1991)
- [16] Grains, growth, and grooving; M.J. Rost et al.; Phys. Rev. Lett. **91**, 026101 (2003)
- [17] Current-Voltage characteristics of self-assembled monolayers by scanning tunneling microscopy; S. Datta et al.; Phys. Rev. Lett. **79**, 2530 (1997)
- [18] Boron nitride nanomesh; M. Corso et al.; Science **303**, 217 (2004)
- [19] High-resolution scanning tunneling microscopy imaging of mesoscopic graphene sheets on an insulating surface; E. Stolyarova et al.; Proceedings of the Nat. Acad. of Sci. of the USA **104**, 9209 (2007)
- [20] Electrochemical STM observation of [Fe(CN)₆]³⁻ ions adsorbed on a hydrotalcite crystal surface; K. Yao et al.; Journ. Electroanalytical Chem. **458**, 249 (1998)
- [21] Electrochemical STM investigation of 1,8-octanedithiol monolayers on Au(111): Experimental and theoretical study; M.J. Esplandiu et al.; Surf. Sci. **600**, 155 (2006)
- [22] High temperature electrochemical scanning tunneling microscope instrument; A. Shkurankov et al.; Rev. Sci. Instr. **73**, 102 (2002)
- [23] New model catalysts (platinum nanoparticles) and new techniques (SFG and STM) for studies of reaction intermediates and surface restructuring at high pressures during catalytic reactions; G.A. Somorjai; Appl. Surf. Sci. **121 - 122**, 1 (1997)
- [24] Surface Science, an introduction; J.B. Hudson; John Wiley & Sons, Inc. (1998)
- [25] Eley-Rideal type mechanism for Formate Synthesis on a Cu(III) surface; J. Ogawa et al.; Nippon Kagakkai Koen Yokoshu **81**, 270 (2002)
- [26] Oxidations carried out by means of vanadium oxide catalysts; P. Mars, and D.W. Van Krevelen, Spec. Suppl. te Chem. Eng. Sci. **3**, 41 (1954)



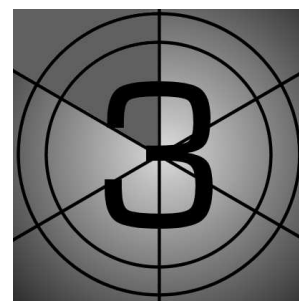
- [27] CO Oxidation on Pt(110): Scanning Tunneling Microscopy Inside a High-Pressure Flow Reactor; B.L.M. Hendriksen, and J.W.M Frenken, *Phys. Rev. Lett.* **89**, 046101 (2002)
- [28] The role of steps in surface catalysis and reaction oscillations; B.L.M. Hendriksen et al.; *Nature Chemistry* **2**, 730 (2010)
- [29] CO oxidation at Pd(100): a first-principles constrained thermodynamics study; J. Rogal et al.; *Phys. Rev. B* **75**, 205433 (2007)
- [30] CO oxidation on Pd(100) at technologically relevant pressure conditions: First-principles kinetic Monte Carlo study; J. Rogal et al.; *Phys. Rev. B* **77**, 155410 (2008)
- [31] Catalysis of gold nanoparticles deposited on metal oxides; M. Haruta; *Cattech* **6**, 102 (2002)
- [32] On the origin of the catalytic activity of gold nanoparticles for low-temperature CO oxidation; N. Lopez et al.; *J. of Cat.* **223**, 232 (2004)
- [33] Steuern Größenquantisierungseffekte die CO adsorption auf Au-Nanopartikeln?; C. Lemire et al.; *Angew. Chem.*, 118 (2003)
- [34] CO Oxidation on Pt-Group Metals from Ultrahigh Vacuum to Near Atmospheric Pressures. 1. Rhodium; F. Gao et al.; *Journ. Phys. Chem. C* **2009**, 182 (2009)
- [35] Highly active surfaces for CO oxidation on Rh, Pd, and Pt; M.S. Chen et al.; *Surf. Sci.* **601**, 5326 (2007)
- [36] Structure and Reactivity of Surface Oxides on Pt(110) during Catalytic CO Oxidation; M.D. Ackermann et al.; *Phys. Rev. Lett* **95**, 255505 (2005)
- [37] Solid state physics; J.R. Hook and H.E. Hall; J. Wiley and sons (2003)
- [38] Chemistry of the elements (2nd ed.); N.N. Greenwood and A. Earnshaw; Butterworth-Heinemann (1997)
- [39] Surface science – an introduction; K. Oura et al.; Springer-Verlag Berlin (2003)
- [40] Common origin for surface reconstruction and the formation of chains of metal atoms; R.H.M. Smit et al.; *Phys. Rev. Lett* **87**, 266102 (2001)



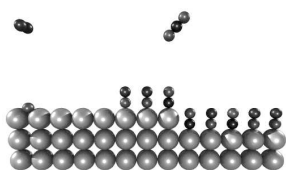
- [41] Relativistic effects in structural chemistry; P. Pyykkö; *Chem. Rev.* **88**, 563 (1988)
- [42] First-principles calculations of equilibrium ground-state properties of Au and Ag; N. Takeuchi et al.; *Phys. Rev. B* **40**, 1565 (1989)
- [43] Reconstruction mechanism of fcc transition-metal (001) surfaces; V. Fiorentini et al.; *arXiv-cond.mat*, May 24 (1993)
- [44] Energy minimization methods in computer vision and pattern recognition; A.K. Jain et al. (editors); (Springer, 2001)
- [45] High-Pressure XPS of Pd model hydrogenation catalysts; D. Teschner et al.; *J. Cat.* **230**, 186 (2005)
- [46] A differentially pumped electrostatic lens system for photoemission studies in the millibar range; D. Ogletree et al.; *Rev. Sci. Instr.* **73**, 3872 (2002)
- [47] Xingcai Su, P. S. Cremer, Y. Ron Shen, and G.A. Somorjai, *J. Am. Chem. Soc.* **1997**, 119, 3994 (1997)
- [48] Oxidation of Pd(553): From ultrahigh vacuum to atmospheric pressure; R. Westerström et al.; *Phys. Rev. B* **76**, 155410 (2007)
- [49] Catalytic CO oxidation over ruthenium bridging the pressure gap; H. Over et al.; *Progress in Surf. Sci.* **72**, 3 (2003)
- [50] A high pressure, high temperature, scanning tunneling microscope for in situ studies of catalysts; B.L. Weeks et al.; *Rev. Sci. Instr.* **71**, 10, 3777 (2000)
- [51] Atomic-scale electron microscopy at ambient pressure; J.F. Creemer et al.; *Ultramicroscopy* **108**, 9, 993 (2008)
- [52] Ultrahigh vacuum/high-pressure flow reactor for surface X-ray diffraction and grazing incidence small angle X-ray scattering studies close to conditions for industrial catalysis; R. van Rijn et al.; *Rev. Sci. Instr.* **81**, 014101 (2010)
- [53] The “Reactor STM”: A scanning tunneling microscope for investigation of catalytic surfaces at semi-industrial reaction conditions; P.B. Rasmussen et al.; *Rev. Sci. Instr.* **69**, 3879 (1998)



- [54] A new scanning tunneling microscope reactor used for high-pressure and high-temperature catalysis studies; F. Tao et al.; *Rev. Sci Instr* **79**, 084101 (2008)
- [55] ReactorAFM: Ultrahigh vacuum/high-pressure flow reactor for atomic force microscopy studies close to conditions for industrial catalysis; M.E. Cañas-Ventura et al.; in preparation for submission to *Rev. Sci. Instr.*
- [56] *Introduction to Scanning Tunneling Microscopy*; C. J. Chen Oxford University Press (1993)
- [57] www.realnano.nl
- [58] High-pressure STM study of NO reduction by CO on Pt(100); C.T. Herbschleb et al.; *Cat. Today* **154**, 61 (2010)
- [59] Kinetics and selectivity of the FischerTropsch synthesis: A literature review; G.P. van der Laan et al; *Catal. Rev.* **41**, 255 (1999)
- [60] An overview of hydrodesulfurization and hydrodenitrogenation; I. Mochida et al.; *Journal of the Japan Petroleum Institute* **47**, 3 (2004)
- [61] VG Scienta (www.vgscienta.com)
- [62] UHV gate valve series 10, VAT (www.vatvalve.com)
- [63] Valcon 75 plus, starcell 150/300, Varian (www.varian.com)
- [64] Turbomolecular pump TPH 261PC in combination with DUO 20 MC, Pfeiffer (www.pfeiffer-vacuum.com)
- [65] Hemi Heating, custom made (www.hemiheating.se)
- [66] XPS Phoibos, SPECS (www.specs.de)
- [67] Model IG35/70, OCI Vacuum Micro-engineering (www.ocivm.com)
- [68] Mini e-beam evaporator EGCO4, Oxford Applied Research (www.oaresearch.co.uk)
- [69] SpectaLEED 4 grid optics with Auger, Omicron (www.omicron.de)
- [70] Vibration Control System, Newport (www.newport.com)
- [71] Custom part, ERIKS (www.eriks.com)



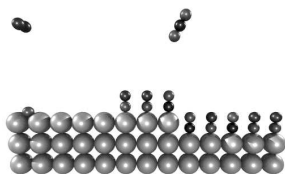
- [72] Zerodur (thermal expansion $\sim 0.02 \cdot 10^{-6} \text{ mK}^{-1}$), Louwers (www.louwers.nl)
- [73] SmCo magnet, IBS Magnet (www.ibsmagnet.com)
- [74] EBL2, Boston Piezo Optics (www.bostonpiezooptics.com)
- [75] Electronics, Leiden Probe Microscopy (www.leidenprobemicroscopy.com)
- [76] Controlling chemical turbulence by global delayed feedback: Pattern formation in catalytic CO oxidation; M. Kim et al.; *Science* **292**, 1357 (2001)
- [77] Microfacetting of a Pt(110) surface during catalytic CO oxidation; S. Ladal et al.; *Surf. Sci.* **197**, 153 (1988)
- [78] CO oxidation on a Pt(110) single crystal surface; H.P. Bonzel et al.; *J. Vac. Sci. and Tech.* **9**, 663 (1972)
- [79] Mechanisms of the catalytic CO oxidation on Pt(110); H.P. Bonzel et al.; *Surf. Sci.* **33**, 91 (1972)
- [80] Subsurface oxygen in the CO-oxidation on Pt(110): Experiment and modeling of pattern formation; A. van Oertzen et al.; *J. Phys. Chem B* **102**, 4966 (1998)
- [81] Kinetic oscillations and facetting during the catalytic CO oxidation on Pt(110); S. Ladas et al.; *Surf. Sci.* **198**, 42 (1988)
- [82] Calorimetric measurement of catalytic surface reaction heat: CO oxidation on Pt(110); C.E. Wartnaby et al.; *J. Chem. Phys.* **102**, 1855 (1995)
- [83] I. Taminiau; Master's thesis, Leiden University (2009)
- [84] EL-flow and EL-press series, Bronkhorst (www.bronkhorst.com)
- [85] Basisboek Vacuümtechniek; E.P.Th.M. Schuurmeijer et al.; NEVAC (2000)
- [86] 37. T-W. Hui, www.chembio.uoguelph.ca
- [87] CRC Handbook of Chemistry and Physics, Lide, 88th edition (2007-2008)



- [88] MEMS-based high-speed scanning probe microscopy; E.C.M. Disseldorp et al.; *Rev. Sci. Instr.* **81**, 043702 (2010)
- [89] Relaxations in the missing-row structure of the (1x2) reconstructed surfaces of Au(110) and Pt(110); E. Vlieg et al.; *Surf. Sci.* **233**, 248 (1990)
- [90] Surface diffusion potential energy surfaces from first principles: CO chemisorbed on Pt(110); Q. Ge et al.; *Journ. Of Chem. Phys.* **111**, 9461 (1999)
- [91] Nitric oxide catalysis in automotive exhaust systems; K.C. Taylor; *Catal. Rev.* **35**, 457 (1993)
- [92] Automobile exhaust catalysts; R.M. Heck et al.; *Applied Catalysis* **221**, 443 (2001)
- [93] Catalytic removal of NO; V.I. Pârvulescu et al.; *Cat. Today* **46**, 233 (1998)
- [94] The surface science approach toward understanding automotive exhaust conversion catalysis at the atomic level; B.E. Nieuwenhuys; *Advances in Catalysis* **44**, 259 (2000)
- [95] The NO+CO reaction on Pt(100); M.W. Lesley et al.; *Surf. Sc.* **155**, 215 (1985)
- [96] A TPD study of NO decomposition on Pt(100), Pt(411) and Pt(211); J.M. Gohndrome et al.; *Surf. Sci.* **209**, 44 (1989)
- [97] Surface restructuring dynamics in CO adsorption, desorption and reaction with NO on Pt(100); A. Hopkinson et al.; *Chem. Phys.* **177**, 433 (1993)
- [98] Bifurcation analysis of the three-variable model for the NO+CO reaction on Pt surfaces; R. Imbihl et al.; *J. Chem. Phys.* **96**, 6236 (1992)
- [99] Energetics and kinetics of CO and NO adsorption on Pt(100): restructuring and lateral interactions; Y.Y. Yeo et al.; *J. Chem. Phys.* **104**, 3810 (1996)
- [100] The temperature dependence of the interaction of NO+CO on Pt(100); J.H. Miners et al.; *Surf. Sci.* **547**, 355 (2003)



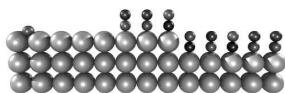
- [101] Defects on the Pt(100) surface and their influence on surface reactions – A scanning tunneling microscopy study; W. Höslér et al.; IBM J. Res. Develop. **30**, 403 (1986)
- [102] Direct observation of a nucleation and growth process on an atomic scale; E. Ritter et al.; Surf. Sci. **181**, 403 (1987)
- [103] Synchrotron XPS and desorption study of the NO chemistry on a stepped Pt surface; C.J. Weststrate et al.; Surf. Sci. **600**, 1991 (2006)
- [104] NO reduction by CO over automotive exhaust gas catalysts in the presence of O₂; J.M.A. Harmsen et al.; Cat. Lett. **71**, 81 (2001)
- [105] 3D atom probe study of gas adsorption and reaction on alloy catalyst surfaces II: results on Pt and Pt-Rh; P.A.J. Bagot; Surf. Sci. **601**, 2245 (2007)
- [106] An experimental test of various models of the active site for NO Reduction on Platinum; R.I. Masel; Cat. Rev. **28**, 335 (1986)
- [107] The mechanism of the explosive NO + CO reaction on Pt(100): experiments and mathematical modelling; T. Fink et al.; Surf. Sci. **245**, 96 (1991)
- [108] Lattice-gas model mimicking the NO+CO reaction on Pt(100); B. Meng et al.; J. Chem. Phys. **101**, 3234 (1994)
- [109] Delay-induced chaos in catalytic surface reactions: NO reduction on Pt(100); N. Khrustova et al.; Phys. Rev. Lett. **75**, 3564 (1995)
- [110] NO reduction by CO on a Pt(100) surface – a DFT study; A. Eichler et al.; Journal of Catalysis **204**, 118 (2001)
- [111] Study of oscillations and pattern formation in the NO+CO reaction on Pt(100) surfaces through dynamic Monte Carlo simulation: Toward a realistic model; S.J. Alas et al.; J. Phys. Chem B **110**, 9499 (2006)
- [112] High pressure STM studies of oxidation catalysis; S.C. Bobaru; Thesis, Leiden University (2006)
- [113] High pressure STM studies of CO + O₂ on Pt(100); S.C. Bobaru et al.; In preparation
- [114] Mechanism and dynamics of the CO-induced lifting of the Pt(100) surface reconstruction; P. van Beurden et al.; Phys. Rev. Lett. **90**, 066106 (2003)



- [115] Kinetic oscillations in the NO+CO reaction on Pt(100): Experiments and mathematical modeling; T. Fink et al.; J. Chem. Phys. **95**, 2109 (1991)
- [116] The superstructures of the clean Pt(100) and Ir(100) surfaces; P. Heilmann et al.; Surf. Sci. **83**, 487 (1979)
- [117] The effect of the surface structure of Pt on its electronic properties and the adsorption of CO, O₂ and H₂: a comparison of Pt(100)-(5x20) and Pt(100)-(1x1); C.R. Helms et al.; J. Chem. Phys. **65**, 1773 (1976)
- [118] Density functional theory (DFT) and microcalorimetric investigations of CO adsorption on Pt clusters; R.M. Watwe et al.; Cat. Lett. **51**, 139 (1998)
- [119] Direct observation of a nucleation and growth process on an atomic scale; E. Ritter et al.; Surf. Sci. **181**, 403 (1987)
- [120] Homoepitaxial growth of Pt on Pt(100)-hex: effects of strongly anisotropic diffusion and finite island sizes; T.R. Linderoth et al.; Phys. Rev. Lett. **77**, 87 (1996)
- [121] STM studies of clean, CO and O₂-exposed Pt(100)-hex-R0.7°; A. Borg et al.; Surf. Sci. **306**, 10 (1994)
- [122] Program LH-fits; EK studios (2008)
- [123] Data reduction and error analysis for the physical sciences; P.R. Bevington et al.; McGraw-Hill (1992)
- [124] Model catalysts in action; B.L.M. Hendriksen; PhD thesis, University of Leiden (2003)
- [125] Operando SXRD: a new view on catalysis; M.D. Ackermann; PhD thesis, University of Leiden and ESRF Grenoble (2007)
- [126] Direct observations of the (1x2) surface reconstruction on the Pt(110) plane; G.L. Kellogg; Phys. Rev. Lett. **55**, 2168 (1985)
- [127] Adsorption-induced step formation; P.Thostrup et al.; Phys. Rev. Lett. **87**, 126102 (2001)
- [128] An STM investigation of the structure of the Pt(110) and Au(110) surfaces; T. Gritsch et al.; Surf. Sci. **257**, 297 (1991)



- [129] Strong bonding of single C_{60} molecules to (1x2)-Pt(110): an STM/DFT investigation; M. Casarin et al.; *J. Phys. Chem.* **2007**, 9365 (2007)
- [130] Shape and decay of 2 and 3 dimensional islands on Au(110); M.J. Rost et al.; *Surf. Sci.* **515**, 344 (2002)
- [131] Shape and evolution of vacancy islands on a MRR surface: Au(110); M.J. Rost et al.; *Surf. Sci.* **518**, 21 (2002)
- [132] Regulation (EC) No 715/2007 of the European parliament and of the council; *Official Journal of the European Union*, L 171/1 (2007)
- [133] *The chemistry and technology of petroleum*; J.G. Speight; Marcel Dekker (1999)
- [134] Present state of the art and future challenges in the hydrodesulphurization of polyaromatic sulfur compounds; D.D. Whitehurst et al.; *Adv. in Cat.* **42**, 345 (1998)
- [135] *Advances in deep desulphurization*; H. Topsøe et al.; *Studies in Surf. Sci. and Cat.* **121**, 13 (1999)
- [136] *The international crude oil market handbook*; Energy Intelligence Group (2004)
- [137] US Energy Information Administration; <http://tonto.eia.doe.gov>
- [138] Genesis Group; <http://www.genesisny.net>
- [139] *Petroleum refining technology and economics*; J.H. Gary et al.; Marcel Dekker (1984)
- [140] *Hydrotreating catalysis, science and technology, vol. 11*; H. Topsøe et al.; Springer Verlag Berlin (1996)
- [141] *Hydrotreating model catalysts: from characterization to kinetics*; L. Coulier; PhD Thesis, Eindhoven technical university (TuE) (2001)
- [142] *Correlating structure and reactivity: MoS₂ nanoparticles for hydrogen evolution*; K.P. Jørgensen; PhD thesis, Technical university of Denmark (2007)
- [143] *Atomic-scale study of a hydrodesulfurization model catalyst*; J.V. Lauritsen; PhD thesis, Århus univesity (2002)



- [144] EU environmental laws impact fuels' requirements; S.F. Venner et al.; *Hydrocarbon Processing* **79** (2000)
- [145] Scanning tunneling microscopy studies on model systems relevant for heterogeneous catalysis; S. Helveg; PhD thesis, Århus university (2000)
- [146] Private communication with Sonja Eijsbouts, Albemarle Catalysts BV
- [147] Hydrodesulfurization catalysis by transition metal surfaces; T.A. Pecoraro et al.; *Journ. of Cat.* **67**, 430 (1981)
- [148] The adsorption and binding of thiophene, butene, and H₂S on the basal plane of MoS₂ single crystals; M. Salmeron et al.; *Chem. Phys. Lett.* **90**, 105 (1982)
- [149] Scanning tunneling microscopy investigations of cluster sizes of molybdenum-based catalysts on graphite; H. Permana et al.; *Cat. Lett.* **24**, 363 (1994)
- [150] Interpretation of STM images: the MoS₂ surface; A. Altibelli et al.; *Surf. Sci.* **367**, 209 (1996)
- [151] Mobile promoters on anisotropic catalysts: nickel in MoS₂; J.G. Kushmerick et al.; *J. Phys. Chem. B* **102**, 10094 (1998)
- [152] Atomic-scale structure of single-layer MoS₂ nanoclusters; S. Helveg et al.; *Phys. Rev. Lett.* **84**, 951 (2000)
- [153] Hydrodesulfurization reaction pathways on MoS₂ nanoclusters revealed by scanning tunneling microscopy; J.V. Lauritsen et al.; *Journ. of Cat.* **224**, 94 (2004)
- [154] Identification of active edge sites for electrochemical H₂ evolution from MoS₂ nanocatalysts; T.F. Jaramillo et al.; *Science* **317**, 100 (2007)
- [155] Structure-function relations in molybdenum sulfide catalysts: the "rim-edge" model; M. Daage et al.; *Journ. of Cat.* **149**, 414 (1994)
- [156] The relation between morphology and hydrotreating activity for supported MoS₂ particles; E.J.M. Hensen; *Journ. of Cat.* **199**, 224 (2001)
- [157] Adsorption of thiophene on the catalytically active surface of MoS₂: an ab initio local-density-functional study; P. Raybaud et al.; *Phys. Rev. Lett.* **80**, 1481 (1998)



- [158] Edge termination of MoS₂ and CoMoS catalyst particles; L.S. Byskov et al.; *Cat. Lett.* **64**, 95 (2000)
- [159] One-dimensional metallic edge states in MoS₂; M.V. Bollinger et al.; *Phys. Rev. Lett.* **87**, 196803 (2001)
- [160] Ab-initio study of the H₂-H₂S/MoS₂ gas-solid interface: the nature of the catalytically active sites; P. Raybaud et al.; *Journ. of Cat.* **189**, 129 (2000)
- [161] Scanning tunneling microscopy observations on the reconstructed Au(111) surface: atomic structure, long-range super structure, rotational domains, and surface defects; J.V. Barth et al.; *Phys. Rev. B* **42**, 9307 (1990)
- [162] Theory of surface stress and surface reconstruction; R.J. Needs et al.; *Surf. Sci.* **242**, 215 (1991)
- [163] Q. Liu et al.; in preparation
- [164] Shape and edge sites modifications of MoS₂ catalytic nanoparticles induced by working conditions: a theoretical study; H. Schweiger et al.; *Journ. of Cat.* **207**, 76 (2002)
- [165] Vacancy formation on MoS₂ hydrodesulfurization catalyst: DFT study of the mechanism; J-F. Paul et al.; *J. Phys. Chem. B* **107**, 4057 (2003)
- [166] Electronic structure and scanning-tunneling-microscopy image of molybdenum dichalcogenide surfaces; K. Kobayashi et al.; *Phys. Rev. B* **51**, 17085 (1995)
- [167] Quartz Microbalance, Inficon (www.inficon.com)
- [168] RC6 Chemical resistant pump, Vacuubrand (www.vacuubrand.com)
- [169] Firerod Cartridge heater; 3 mm diameter, 3 cm long. Watlow bv. (www.watlow.com)
- [170] Imaging and modification of Au(111) monatomic steps with atomic force microscopy; C.A. Goss et al.; *Langmuir* **1993**, 2986 (1993)
- [171] Structure and function of the catalyst and the promoter in Co-Mo hydrodesulfurization catalysts; R. Prins et al.; *Cat. Rev.-Sci. Eng.* **31**, 1 (1989)



- [172] Spectroscopy in catalysis; J.W. Niemantsverdriet; 2nd ed (Wiley-VCH Verlag GmbH, Weinheim, 2000)
- [173] Genesis, architecture and nature of Co(Ni)-MoS₂ supported hydroprocessing catalysts; J. Grimblot; *Cat. Tod.* **41**, 111 (1998)
- [174] Hydrodesulphurization and hydrogenation; T.K. Qian (Wiley New York, 1999)
- [175] Size-dependent structure of MoS₂ nanocrystals; J.V. Lauritsen et al.; *Nature Nanotechnology* **2**, 53 (2007)
- [176] The hydrogenation and direct desulphurization reaction pathway in thiophene hydrodesulphurization over MoS₂ catalysts at realistic conditions: a density functional theory study; P.G. Moses et al.; *Journ. Cat* **248**, 188 (2007)
- [177] Recent STM, DFT and HAADF-STEM studies of sulphide-based hydrotreating catalysts: insight into mechanistic, structural and particle size effects; F. Besenbacher et al.; *Cat. Today* **130**, 86 (2008)
- [178] D. Costa et al.; Edge wetting effects of γ -Al₂O₃ and anatase-TiO₂ supports by MoS₂ and CoMoS active phase: A DFT study; *J. Cat.* **246**, 325 (2007)
- [179] Reactivities in deep catalytic hydrodesulfurization: challenges, opportunities, and the importance of 4-methyldibenzothiophene and 4, 6-dimethyldibenzothiophene; B.C. Gates et al.; *Polyhedron* **16**, 3213 (1997)
- [180] Atomic scale insight into structure and morphology changes of MoS₂ nano-clusters in hydrotreating catalysis; J.V. Lauritsen et al.; *Journ. Cat* **221**, 550 (2004)
- [181] Ab initio DFT study of H₂ dissociation on MoS₂, NiMoS and CoMoS: mechanism, kinetics and vibrational frequencies; M. Sun et al.; *Journ. Cat.* **233**, 411 (2005)
- [182] An EXAFS study of the structure of supported cobalt molybdate catalysts as a function of sulfiding temperature; T.G. Parham et al.; *J. Cat.* **85**, 295 (1984)
- [183] The crystal structure of molybdenite; R.G. Dickinson et al.; *J. Am. Chem. Soc.* **45**, 1466 (1923)



- [184] A geometrical model of the active phase of hydrotreating catalysts; S. Kasztelan et al.; *Appl. Cat.* **13**, 127 (1984)
- [185] The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties; J.A. Wilson et al.; *Adv. in Phys.* **18**, 193 (1969)
- [186] A symmetry principle for epitaxial rotation; F. Grey et al.; *Europhys. Lett.* **18**, 717 (1992)
- [187] On the catalytic significance of a Co-Mo-S phase in Co-Mo/Al₂O₃ hydrodesulfurization catalysts: combined in situ Mössbauer emission spectroscopy and activity studies; C. Wevel et al.; *Journ. of Cat.* **68**, 453 (1981)
- [188] Structure, energetics and electronic properties of the surface of a promoted MoS₂ catalyst: an ab initio local density functional theory study; P. Raybaud et al.; *Journ. Cat.* **190**, 128 (2000)
- [189] Reactivity studies with gold-supported molybdenum nanoparticles; D.V. Potapenko et al.; *Surf. Sci.* **574**, 244 (2005)
- [190] Surface alloying of immiscible metals: Mo on Au(111) studied by STM; M.M. Biener et al.; *Surf. Sci.* **594**, 221 (2005)
- [191] Interaction of CO, O, and S with metal nanoparticles on Au(111): A theoretical study; Ping Liu et al.; *Phys. Rev. B* **67**, 155416 (2003)
- [192] Density Functional Theory study of CO adsorption on Molybdenum Sulfide; Tao Zeng et al.; *J. Phys. Chem. B* **109**, 2846 (2005)
- [193] Number taken from the website of OICA (Organisation Internationale des Constructeurs d'Automobiles), <http://oica.net>



Index

- adsorption, 8
 - associative, 9
 - dissociative, 9
- Au(111), 94
- Catalysis, 7
 - Heterogeneous, 7
 - History, 6
 - Homogeneous, 7
 - Traditional research, 12
- Chemical potential μ , 13
- Crystallography
 - Crystal structures, 20
 - Miller indices, 20
 - Reconstruction, 22
 - Au(111), 108
 - Pt(100), 52
 - Pt(110), 71, 77
 - Relaxation, 22
 - Unit cell, 17
- Curriculum Vitae, 126
- Dutch summary, 119
- English summary, 116
- Fuel
 - (Deep) desulphurization, 84
 - Hydrotreating, 83
 - Legislation, 83
- Gas manifold
 - Layout Mark II manifold, 40
 - Mark I manifold, 27
 - Mark II manifold, 37, 42
- Gold-molybdenum alloying, 112
- Hydrodesulphurization
 - Batch experiment, 99
 - Control experiment, 99
- Langmuir theorem of adsorption, 9
- Materials gap, 14
- Moiré pattern
 - MoS₂ on Au(111), 105
 - Pt(100), 52
 - theory, 22
- Molybdenum disulphide, 85, 104
 - Bias voltage effect, 103
 - Bright rim, 87
 - Preparation, 95
 - Reaction pathways, 89
 - Structure, 86
- molybdenum disulphide
 - Edges, 88
- NO reduction, 48
 - χ^2_ν test, 65
 - Dual kinetics fit, 65
 - Rate equations, 50
 - Rate equations derivation, 67
 - Reaction constants, 51
 - Single kinetics fit, 63
- Platinum
 - Pt(100), 49, 52
 - Pt(110), 71
- Pressure gap, 13
- Pt(110) (1x2) oxide, 73, 78



- Reaction mechanisms, 10
 - Eley-Rideal, 11
 - Langmuir-Hinshelwood, 10, 64
 - Mars-Van Krevelen, 11
- ReactorSTM
 - Approach and scan actuator, 34
 - Concept, 25
 - Mark I adjustments, 92
 - Mark II UHV system, 31, 42
 - Mass spectrometry, 41
 - Specs list, 30
 - STM insert flange, 34
 - The Mark I, 25
 - The Mark II, 33, 43
 - Tip quality, 81
- Research techniques in catalysis
 - AFM, 17
 - IRAS, 15
 - STM, 16
 - SXRD, 16
 - TEM, 16
 - XPS, 15
- Scanning Tunneling Microscopy, 23