



Universiteit  
Leiden

The Netherlands

## Understanding the surface structure of catalysts and 2D materials at the atomic scale

Boden, D.

### Citation

Boden, D. (2023, September 12). *Understanding the surface structure of catalysts and 2D materials at the atomic scale*.

Version: Publisher's Version

License: [Licence agreement concerning inclusion of doctoral thesis in the Institutional Repository of the University of Leiden](#)

Downloaded from:

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

# Understanding the Surface Structure of Catalysts and 2D Materials at the Atomic Scale

Proefschrift

ter verkrijging van  
de graad van doctor aan de Universiteit Leiden,  
op gezag van rector magnificus prof.dr.ir. H. Bijl,  
volgens besluit van het college voor promoties  
te verdedigen op dinsdag 12 september 2023  
klokke 13:45 uur

door

Dajo Boden  
geboren te Amsterdam, Nederland  
in 1995

**Promotor:** Dr. I.M.N. Groot

**Co-promotor:** Dr. J. Meyer

**Promotiecommissie:** Prof. Dr. M. Ubbink  
Prof. Dr. Ir. T.H. Oosterkamp  
Prof. Dr. G.S. Parkinson Technische Universitat Wien  
Prof. Dr. T. Jacob Universitat Ulm  
Dr. K. Doblhoff-Dier

The research described in this thesis has been performed at, and funded by, the Leiden Institute of Chemistry (Einsteinweg 55, 2333 CC, Leiden).

This work has been supported by the Dutch Organization for Scientific Research (NWO) and the SURF Cooperative, by providing computing time on the Cartesius and Snellius facilities (Grant 17216).

ISBN: 978-94-6469-425-3

# Table of Contents

<b>1</b>	<b>Introduction</b>	<b>1</b>
1.1	The Surface-Science Approach - a Success Story . . . . .	2
1.2	The Gaps Between Theory and Experiment . . . . .	3
1.3	Towards Closing the Gaps . . . . .	4
1.3.1	A Comprehensive Description of the Surface . . . . .	4
1.3.2	Considering Finite Temperature and Pressure . . . . .	5
	References . . . . .	7
<b>2</b>	<b>Experimental Methods</b>	<b>11</b>
2.1	Ultra-high Vacuum . . . . .	12
2.2	Low-Energy Electron Diffraction . . . . .	12
2.3	Electron Spectroscopy . . . . .	14
2.3.1	Auger Electron Spectroscopy . . . . .	14
2.3.2	X-ray Photoelectron Spectroscopy . . . . .	15
2.4	Scanning Tunneling Microscopy . . . . .	16
2.5	The ReactorSTM Setup . . . . .	18
2.5.1	Sample Holder . . . . .	18
2.5.2	Analysis Chamber . . . . .	19
2.5.3	Sample Preparation Chamber . . . . .	19
2.5.4	STM Chamber . . . . .	19
2.6	Sample Preparation . . . . .	20
2.6.1	Sample Cleaning . . . . .	20
2.6.2	Electron-Beam Physical Vapor Deposition . . . . .	21
	References . . . . .	22
<b>3</b>	<b>Theoretical Methods</b>	<b>23</b>
3.1	Electronic Structure Calculations . . . . .	24
3.1.1	Born-Oppenheimer Approximation . . . . .	24
3.1.2	Density-Functional Theory . . . . .	24
3.1.3	Analyzing Charge Transfer . . . . .	25
3.2	Simulating STM Images . . . . .	26
3.2.1	Bardeen's Formalism . . . . .	26
3.2.2	Tersoff-Hamann Approach . . . . .	30
3.3	Atomistic Thermodynamics . . . . .	32
	References . . . . .	36

---

<b>4</b>	<b>Structural Characterization of a Novel 2D Material: Cobalt Sulfide Sheets on Au(111)</b>	<b>39</b>
4.1	Introduction . . . . .	40
4.2	Experimental Methods . . . . .	41
4.3	Theoretical Methods . . . . .	41
4.4	Results & Discussion . . . . .	42
4.5	Conclusions . . . . .	48
	References . . . . .	49
<b>5</b>	<b>Elucidating the Initial Oxidation of Pt(111) Using Large-Scale Atomistic Thermodynamics: a ReaxFF Study</b>	<b>51</b>
5.1	Introduction . . . . .	53
5.2	Methods . . . . .	55
5.2.1	Atomistic Thermodynamics . . . . .	55
5.2.2	Computational Details . . . . .	56
5.3	Results and Discussion . . . . .	57
5.3.1	ReaxFF Benchmark for PtO <sub>2</sub> Stripes . . . . .	57
5.3.2	Spoke-wheel Structure . . . . .	59
5.3.3	Implications for the Initial Oxidation of Pt(111) . . . . .	63
5.4	Conclusions and Outlook . . . . .	65
	References . . . . .	67
<b>6</b>	<b>The Effect of NO and CO on the Rh(100) Surface at Atmospheric Pressure</b>	<b>69</b>
6.1	Introduction . . . . .	70
6.2	Methods . . . . .	73
6.2.1	Experimental Methods . . . . .	73
6.2.2	Computational Methods . . . . .	74
6.3	Results and Discussion . . . . .	74
6.3.1	High-pressure CO . . . . .	74
6.3.2	High-pressure NO . . . . .	80
6.3.3	High-pressure CO + NO . . . . .	83
6.3.4	Theory . . . . .	85
6.4	Conclusion . . . . .	90
6.5	Outlook . . . . .	90
	References . . . . .	92
<b>7</b>	<b>Summary &amp; Outlook</b>	<b>97</b>
	References . . . . .	101
	<b>Appendices</b>	<b>103</b>
<b>A</b>	<b>Chapter 2: Experimental Methods</b>	<b>105</b>
A.1	Capacitive Approach . . . . .	106
	References . . . . .	109

---

---

<b>B Chapter 4: Structural Characterization of a Novel 2D Material: Cobalt Sulfide Sheets on Au(111)</b>	<b>111</b>
B.1 Au(111) Exposed to H <sub>2</sub> S . . . . .	112
B.2 2D Cobalt Sulfide Sheets of Various Sizes Supported on Au(111) . . . . .	113
B.3 XPS Spectra . . . . .	115
B.4 TMDC-like Structure in Sulfur-terminated Co <sub>3</sub> S <sub>4</sub> (111) . . . . .	116
B.5 TMDC-like Structure in CoS(0001) . . . . .	119
B.6 Density of States and Band Structure of CoS(0001)/Au(111) . . . . .	120
B.7 Charge Analysis . . . . .	122
B.8 Van-der-Waals Corrections . . . . .	124
References . . . . .	125
<b>C Chapter 5: Elucidating the Initial Oxidation of Pt(111) Using Large-Scale Atomistic Thermodynamics: a ReaxFF Study</b>	<b>127</b>
C.1 Vibrational Frequencies with the Pt-O ReaxFF . . . . .	128
C.2 Most Stable Partially Oxidized PtO <sub>2</sub> -stripe Structures . . . . .	128
References . . . . .	139
<b>D Chapter 6: The Effect of NO and CO on the Rh(100) Surface at Atmospheric Pressure</b>	<b>141</b>
D.1 Step Edges on Clean Rh(100) . . . . .	142
D.2 NO Adsorption on Rh(100) . . . . .	144
D.3 Mixed NO and CO c(2×2) . . . . .	145
D.4 Zero-point Vibrational Energies of NO and CO . . . . .	146
D.5 Structures Used in Figure 6.15 . . . . .	148
D.6 Phase Diagram at 650 K . . . . .	149
References . . . . .	150
<b>Samenvatting</b>	<b>151</b>
<b>List of Publications</b>	<b>153</b>
<b>Curriculum Vitae</b>	<b>154</b>
<b>Acknowledgments</b>	<b>155</b>

