

## Table of contents

List of symbols <sup>a</sup> .....	8
1 Introduction.....	11
1.1 Nanoparticle catalysis.....	11
1.2 Small molecules activation on metal nanoparticle catalysts: the need for model systems.....	12
1.3 Computational first principles modeling of nanoparticle catalysts.....	16
1.3.1 Mechanistic insights for small molecule activation.....	16
1.4 Objectives and outline.....	24
2 Computational Methods.....	26
2.1 Periodic density functional theory.....	26
2.1.1 Density functional theory foundations.....	26
2.1.2 Exchange-correlation functionals.....	27
2.1.3 Periodic boundary conditions and basis sets.....	29
2.1.4 Pseudopotentials.....	32
2.1.5 From bulk to surface slabs and nanoparticle model systems.....	33
2.2 Electronic structure analysis via the projected crystal orbital Hamilton population.....	34
2.3 Nudged elastic band.....	36
2.4 Free energy from density functional theory and statistical mechanics.....	37
2.4.1 Ideal gas.....	38
2.4.2 Adsorbed species.....	40
2.5 Free energy from ab initio molecular dynamics.....	41
2.5.1 Ab initio molecular dynamics.....	42
2.5.2 Free energy calculations.....	43
2.5.3 Metadynamics.....	44
2.6 Microkinetic modeling.....	45
3 Reactivity of Ru step-edge sites towards the direct CO dissociation and particle size effects.....	48

3.1 Increased back-donation explains step-edge reactivity and particle size effect for CO activation on Ru nanoparticles.....	48
3.1.1 Individual contributions.....	48
3.1.2 Abstract.....	48
3.1.3 Introduction.....	49
3.1.4 Computational details.....	50
3.1.5 Results.....	51
3.1.6 Conclusions.....	74
3.2 Electronic structure-reactivity relationship on Ruthenium step-edge sites from carbonyl <sup>13</sup> C chemical shift analysis.....	76
3.2.1 Individual contributions.....	76
3.2.2 Abstract.....	76
3.2.3 Introduction.....	76
3.2.4 Results and discussion.....	78
3.2.5 Conclusions.....	83
4 Dynamic effects on Ru-catalyzed Fischer-Tropsch synthesis mechanisms.....	85
4.1 Adlayer dynamics drives CO activation in Ru-catalyzed Fischer-Tropsch synthesis.....	85
4.1.1 Individual contributions.....	85
4.1.2 Abstract.....	85
4.1.3 Introduction.....	85
4.1.4 Computational section.....	87
4.1.5 Results.....	90
4.1.6 Discussion.....	96
4.1.7 Conclusions.....	98
4.2 Hydrogen-transfers and C-O activation on Ru catalysts: entropy-driven mechanisms revealed by ab initio molecular dynamics.....	100
4.2.1 Individual contributions.....	100
4.2.2 Abstract.....	100
4.2.3 Introduction.....	100

4.2.4	Results and discussion .....	102
4.2.5	Conclusions .....	107
4.3	Carbon-carbon bond formation in Fischer-Tropsch synthesis: carbene coupling mechanism from ab initio molecular dynamics .....	109
4.3.1	Individual contributions .....	109
4.3.2	Abstract .....	109
4.3.3	Introduction .....	109
4.3.4	Computational section .....	112
4.3.5	Results and discussion .....	113
4.3.6	Conclusions .....	127
5	Multi-scale reactivity of metal catalysts for CO <sub>2</sub> conversion processes .....	129
5.1	Intrinsic reactivity of Ni, Pd and Pt surfaces in dry reforming and competitive reactions: Insights from first principles calculations and microkinetic modeling simulations .....	129
5.1.1	Individual contributions .....	129
5.1.2	Abstract .....	129
5.1.3	Introduction .....	130
5.1.4	Computational details .....	132
5.1.5	Results and discussion .....	136
5.1.6	Conclusion .....	153
5.2	Contrasting the role of Ni/Al <sub>2</sub> O <sub>3</sub> interfaces in water-gas shift and dry reforming of methane 155	
5.2.1	Individual contributions .....	155
5.2.2	Abstract .....	155
5.2.3	Introduction .....	155
5.2.4	Computational methods .....	159
5.2.5	Experimental procedures .....	159
5.2.6	Results .....	160
5.2.7	Conclusions .....	175
6	Conclusions .....	177

6.1	Summary .....	177
6.2	Outlook for future work .....	180
6.2.1	Fischer-Tropsch chemistry .....	180
6.2.2	First principles modeling of transition metal catalysts .....	181
6.3	Final remarks .....	183
Appendix 1	.....	184
Appendix 2	.....	199
Appendix 3	.....	216
Appendix 4	.....	228
Appendix 5	.....	235
Appendix 6	.....	242
Appendix 7	.....	253
Bibliography	.....	273