Contents

Acknowledgements 7

Contents 11

Introduction 15

1.1. Catalysis. 16

1.2. Heterogeneous catalysis. 18

1.3. Subnanometer metal clusters in catalysis. 21

1.3.1. Electronic structure of subnanometer metal clusters. 23
1.3.2. Synthesis of atomically precise subnanometer metal clusters. 27
1.3.3. The metal-support interaction (MSI). 31
1.3.4. Identification of the active species. 32

1.4. Motivation. 34

Theoretical background 35

2.1. The Schrödinger equation. 36

2.2. Density Functional Theory. 37

2.3. Models. 45

2.4. Basis sets. 48

2.5. Optimization algorithms. 52

2.6. Steady state analysis. 56

2.7. Thermodynamic properties. 61

2.8. Kinetics and reaction mechanism. 64

O_2 dissociation by gas phase Cu clusters 67

3.1. Introduction. 68

3.2. Computational details. 69

3.3. Results. 71

3.3.1. O_2 dissociation and comparison of methodologies. 71
3.3.2. O_2 dissociation kinetics and comparison with experiment. 100
3.3.3. Influence of H_2O in the O_2 dissociation by Cu clusters. 111

3.4. Conclusions. 116

Oxidation reactions on gas phase Cu clusters 119

4.1. Introduction. 120

4.2. Computational details. 121

4.3. Results. 122

4.3.1. CO oxidation on Cu_n (n = 5, 8) clusters. 122
4.3.2. Propene epoxidation on Cu_5 clusters. 139

4.4. Conclusions. 154

Supported Cu clusters 157

5.1. Introduction. 158

5.2. Computational details. 159

5.3. Results. 160

5.3.1. Graphene-supported copper clusters. 160
5.3.2. Ceria-supported copper clusters. 186

5.4. Conclusions. 203

Heck reaction on Pt_3 and Pd_3 clusters 205

6.1. Introduction. 206

6.2. Computational details. 208

6.3. Results. 209

6.3.1. Background from experiments. 209
6.3.2. Mechanism of the Heck coupling by Pd and Pt clusters. 213

6.4. Conclusions. 227

CO + NO reaction by Pt clusters 229

7.1. Introduction. 230

7.2. Computational details. 231

7.3. Results. 232

7.3.1. Background from experiments. 232
7.3.2. Mechanism of the CO + NO reaction by Pt clusters. 233

7.4. Conclusions. 246

Conclusions 249

Summary 255

Resumen 259

Resum 263
List of Publications 267
References 269