

Contents

List of Figures.....	iv
List of Tables.....	x
CHAPTER 1 Heterogeneous Catalysis: A Sustainable Future	1
1.1 Heterogeneous catalysis.....	2
1.2 Transition-metal nanoclusters and nanoalloys	7
1.2.1 Supported clusters	10
1.3 Reaction mechanism for CO oxidation.....	13
1.4 CO ₂ hydrogenation	14
1.5 Thesis motivation and objectives.....	16
1.6 Thesis organization.....	18
References.....	21
CHAPTER 2 Theoretical Background and Computational Methods	25
2.1 Density functional theory.....	26
2.2 The Kohn-Sham theory.....	29
2.2.1 Exchange and correlation functionals.....	32
2.2.2 Plane-wave and pseudopotentials.....	32
2.2.3 Geometry optimization.....	35
2.2.4 van der Waals corrections.....	36
2.3 Analysis of the electronic properties.....	37
2.3.1 Density of states (DOS)	37
2.3.2 Charge density analysis	39
2.3.3 Electronic reactivity descriptors.....	39
2.4 Density functional perturbation theory.....	41
2.5 Transition state determination.....	42
2.5.1 Regular NEB method	42
2.5.2 Climbing image NEB method.....	43
2.6 Computational codes and visualization softwares.....	44

References.....	46
CHAPTER 3 Poisoning-free CO oxidation over Ni_nCu Cluster	48
3.1 Introduction.....	49
3.2 Computational methods and theoretical analysis.....	51
3.3 Results and Discussion	52
3.3.1 Ni _{n+1} and Ni _n Cu clusters ($1 \leq n \leq 12$)	52
3.3.2 Ni K-edge XANES.....	57
3.3.3 Structural stability and energetics.....	59
3.3.4 CO adsorption over Ni _{n+1} and Ni _n Cu clusters ($1 \leq n \leq 12$)	61
3.3.5 Electronic properties.....	67
3.3.6 Charge density difference.....	75
3.3.7 Work-function analysis.....	76
3.3.8 CO oxidation reaction pathway.....	77
3.4 Conclusions.....	83
References.....	86
CHAPTER 4 Mechanistic insight into Pd_mCu_n Clusters: Implication to the CO₂	
Hydrogenation.....	89
4.1 Introduction.....	90
4.2 Computational details	91
4.3 Results and Discussion	93
4.3.1 Structural stability and electronic properties of I _h Pd _m Cu _n clusters... 93	
4.3.2 Raman spectra of I _h Pd _m Cu _n clusters.....	102
4.3.3 Adsorption of CO ₂ molecule over I _h Pd _m Cu _n clusters.....	105
4.3.4 CO ₂ conversion into hydrocarbon fuels on I _h Pd ₅ Cu ₈ cluster.....	109
4.4 Conclusions.....	121
References.....	124
CHAPTER 5 Determining the CO Oxidation Activity of Supported Pt₃M Clusters	
.....	129
5.1 Introduction.....	130

5.2 Computational details	132
5.3 Results and Discussion	134
5.3.1 Structural and electronic properties of $\text{Cu}_2\text{O}(111)$ surface	134
5.3.2 Pt_4 and Pt_3X ($\text{X} = \text{Co} \ \& \ \text{Au}$) supported on $\text{Cu}_2\text{O}(111)$ surface.....	136
5.3.3 CO adsorption on supported clusters	144
5.3.4 L-H reaction mechanism for CO oxidation.....	146
5.4 Conclusions.....	149
References.....	151
CHAPTER 6 Conclusions and Future Prospects.....	154
6.1 Summary	155
6.2 Future Scope	158
APPENDIX.....	160
A.1 Determination of the lowest-energy structures of Ni_{n+1} clusters.....	161
A.2 Determination of the lowest-energy structures of Ni_nCu clusters	162
A.3 Determination of point-group symmetry (structure) of Ni_{n+1} and Ni_nCu clusters ($1 \leq n \leq 12$)	163
A.4 Determination of structural stability and relative energetics.....	164
A.5 Theoretical analysis of quantum chemical descriptors.	167
A.6 Adsorption energetics of CO on Ni_{n+1} and Ni_nCu clusters.....	170