

STO	Slater type orbital
TM	Transition metal
TS	Transition state
TER	Termolecular Eley Rideal
TLH	Termolecular Langmuir Hinshelwood
XC	Exchange correlation

Table of Contents	Page No.
Abstract	i-v
Declaration by the candidate	vi
Certificate from the supervisor	vii
Certificate of the external examiner	viii
Acknowledgement	ix-xi
Table of Contents	xii-xv
List of Figures	xvi-xx
List of Tables	xxi-xxiv
List of abbreviations	xxv-xxvi
<i>Chapter 1: Introduction of the present work</i>	
1.1 Nanoscience: Definition and Origins	1-1
1.2 Synthesis of nanomaterials	1-4
1.3 Reactivity of nanoparticles	1-5
1.4 Nanoclusters and subnanometre clusters	1-6
1.4.1 Preparation and characterization of small clusters	1-7
1.4.2 Types of clusters	1-7
1.4.3 Importance of transition metal clusters in catalysis	1-8
1.5 Catalytic oxidation of Nitric oxide (NO)	1-9
1.5.1 Importance of small transition metal clusters for catalytic oxidation of NO	1-11
1.6 Catalytic reactions over zeolite supported metal clusters	1-13
1.7 Mechanisms for NO oxidation	1-17
1.8 Objectives of the present work	1-21
1.9 Bibliography	1-21
<i>Chapter 2: Overview of the computational methods</i>	
2.1 Introduction	2-1
2.1.1 Potential Energy Surface (PES)	2-1
2.2 Computational Chemistry Tools	2-3
2.2.1 Molecular Mechanics (MM)	2-3
2.2.1.1 Strength and weakness of MM theory	2-4
2.2.2 Molecular Dynamics (MD)	2-5
2.2.3 Ab-initio Methods	2-5
2.2.3.1 Hartree-Fock Method	2-6
2.2.4 Semi-empirical Method	2-8
2.2.5 Density Functional Theory (DFT)	2-8
2.2.5.1 The Kohn-Sham Formalism	2-10
2.2.5.2 Density Functional Approximations	2-11
2.2.5.3 Basis Set	2-13
2.2.6 The QM/MM ONIOM method	2-14
2.3 Transition state theory	2-15

2.4	Software Packages used to carry out the computational work	2-16
2.4.1	The Gaussian Package	2-16
2.4.2	The Multiwfn Package	2-16
2.5	Bibliography	2-17

Chapter 3: Mechanistic insights on catalytic oxidation of NO to NO₂ on [Pt₂]^{0,±} monometallic dimers using O₂

3.1	Introduction	3-1
3.2	Computational Details and Kinetic Theory	3-3
3.3	Results and Discussion	3-6
3.3.1	Electronic structures and properties of [Pt ₂] ^{0,±} catalyst	3-6
3.3.2	Adsorption and co-adsorption of NO and O ₂ on [Pt ₂] ^{0,±} dimer	3-10
3.3.3	Catalytic oxidation pathway of NO on [Pt ₂] ^{0,±} dimers	3-21
	3.3.3.1 Langmuir Hinshelwood (L-H) mechanism	3-21
	3.3.3.2 Termolecular Eley Rideal (TER) mechanism	3-30
	3.3.3.3 Termolecular Langmuir Hinshelwood (TLH) mechanism	3-38
	3.3.3.4 Thermodynamic and Kinetic analysis	3-43
3.4	Significant Outcomes	3-47
3.5	Bibliography	3-48

Chapter 4: Catalytic Oxidation of NO on [Au-M]⁺ (M=Pd & Pt) Bimetallic Dimers: An Insight from DFT Approach

4.1	Introduction	4-1
4.2	Computational Details and Kinetic Theory	4-3
4.3	Results and Discussion	4-5
4.3.1	Electronic structures and properties of [Au-M] ⁺ (M=Pd, Pt) catalyst	4-5
4.3.2	Adsorption of NO/O ₂ on [Au-M] ⁺ (M=Pd, Pt) dimers	4-9
4.3.3	Co-adsorption of NO/O ₂ on [Au-M] ⁺ (M=Pd, Pt) dimers	4-12
4.3.4	Catalytic oxidation pathway of NO on [Au-M] ⁺ (M=Pd, Pt) dimer	4-18
	4.3.4.1 Langmuir Hinshelwood (L-H) mechanism	4-18
	4.3.4.2 Termolecular Eley Rideal (TER) mechanism	4-23
	4.3.4.3 Termolecular Langmuir Hinshelwood (TLH) mechanism	4-27
	4.3.4.4 Efficiency of clusters using energetic span model	4-31
	4.3.4.5 Kinetic analysis	4-32
4.4	Significant Outcomes	4-34
4.5	Bibliography	4-34

Chapter 5: Mechanistic DFT investigation of catalytic oxidation of NO to NO₂ on pristine and doped [Au_nPd_{3-n}]⁻ (n=0-3) clusters.

5.1	Introduction	5-1
5.2	Computational Details	5-4
5.3	Results and Discussion	5-6
5.3.1	Electronic structures and energies of the [Au _n Pd _{3-n}] ⁻ (n=0-3) clusters	5-6
5.3.2	Molecular orbital analysis and electronic properties of the [Au _n Pd _{3-n}] ⁻ (n=0-3) clusters	5-8
5.3.3	NO/O ₂ adsorption properties on [Au _n Pd _{3-n}] ⁻ (n=0-3) clusters	5-11
5.3.4	Catalytic oxidation pathway of NO on [Au _n Pd _{3-n}] ⁻ (n=0-3) clusters	5-22
5.3.4.1	Langmuir Hinshelwood (L-H) mechanism	5-22
5.3.4.2	Termolecular Eley Rideal (TER) mechanism	5-31
5.3.4.3	Termolecular Langmuir Hinshelwood (TLH) mechanism	5-37
5.3.4.4	Efficiency of clusters using energetic span model	5-42
5.4.	Significant Outcomes	5-44
5.5	Bibliography	5-45

Chapter 6: Adsorption and activation of nitric oxide (NO) and oxygen (O₂) on bare and supported M_n/ZSM-5 [M=Au, Pd, Pt] (n=1-2) using ONIOM method

6.1	Introduction	6-1
6.2	Computational Details	6-3
6.3	Results and Discussion	6-5
6.3.1	Cluster framework interaction energies	6-5
6.3.2	Adsorption of NO and O ₂ on bare and ZSM-5 supported Au _n (n=1-2) system	6-7
6.3.3	Adsorption of NO and O ₂ on bare and ZSM-5 supported Pt _n (n=1-2) system	6-12
6.3.4	Adsorption of NO and O ₂ on bare and ZSM-5 supported Pt _n (n=1-2) system	6-17
6.4.	Significant Outcomes	6-22
6.5	Bibliography	6-23

Chapter 7: Conclusion and Future Prospects

7.1.	Conclusion	7-1
7.2	Future Prospects	7-4
	List of Academic Publications, Book chapters and Conferences attended	xxvii-xxx