

# Contents

<i>Agradecimientos</i> .....	
<i>Contents</i> .....	
<i>Glossary</i> .....	
<b>Chapter 1 Introduction</b> .....	1
1.1 Catalysis .....	2
1.2 Heterogeneous Catalysis .....	10
1.2.1 Steps .....	11
1.2.1.1 Mechanistic Insights.....	13
1.2.2 Solid Catalysts.....	14
1.2.2.1 Crystal Lattices.....	14
1.3 Zeolites and Zeotypes.....	17
1.3.1 Zeolites.....	17
1.3.2 Zeotypes .....	22
1.4 Metal Clusters and the Sub-nanometre realm .....	25
1.4.1 The beginning of Cluster Science .....	25
1.4.2 Metal Clusters: Definition & Properties.....	27
1.5 Brief history of Methane-to-Methanol chemical reaction.....	31
<b>Chapter 2 Computational Chemistry: Theoretical background and Methodology</b> .....	43
2.1 Computational Chemistry: A theoretical field of science .....	44
2.2 The Schrödinger equation .....	46
2.3 The settlement of Density Functional Theory (DFT).....	52
2.3.1 Kohn-Sham self-consistent method.....	55
2.3.2 The quest to find the best approximation to the exchange- correlation functional .....	59

2.3.2.1 Local-density Approximation (LDA).....	60
2.3.2.2 Generalized Gradient Approximation (GGA).....	61
2.3.2.3 Meta-GGAs and Hybrid Functionals .....	62
2.3.2.4 The inclusion of dispersion forces in DFT.....	63
2.4 Basis Sets .....	66
2.4.1 Atom-centred Basis Sets .....	66
2.4.2 Reciprocal Space and Planewaves .....	67
2.4.3 Solutions to the use of Planewaves: Pseudopotentials and the Projector Augmented-wave method (PAW) .....	71
2.5 Potential Energy Surface (PES) .....	74
2.6 The Vienna Ab-initio Simulation Package (VASP).....	76
2.6.1 Minimum States .....	76
2.6.2 Transition States.....	76
2.6.3 Vibrational Analysis.....	78
2.6.4 Free energy.....	80
2.6.5 Charge Analysis .....	82
2.6.6 Reaction Kinetics .....	84
2.7 Models.....	85
2.7.1 Periodic Models.....	86
<b><i>Chapter 3 Selective Oxidation of Methane to Methanol with Molecular O<sub>2</sub> using Sub-nanometre Copper Clusters</i></b> .....	91
3.1 Introduction.....	92
3.2 O <sub>2</sub> dissociation over Cu <sub>n</sub> clusters.....	95
3.3 Methane Oxidation on 2D and 3D Cu <sub>5</sub> Clusters .....	104
3.4 Methane Oxidation on Cu <sub>7</sub> clusters.....	118
3.5 Discussion for both Langmuir-Hinshelwood and Eley-Rideal pathways in Cu <sub>n</sub> clusters .....	129
3.5.1 Cu <sub>5</sub> clusters.....	130
3.5.2 Cu <sub>7</sub> clusters.....	135
3.6 Conclusions .....	142

3.7 Appendix .....	144
<b>Chapter 4 Selective Oxidation of Methane into Methanol over <math>Cu_n</math> Clusters supported within CHA .....</b>	<b>153</b>
4.1 Introduction .....	154
4.2 $O_2$ dissociation over $Cu_n$ -CHA clusters.....	157
4.2.1 Confined $Cu_n$ Clusters .....	157
4.2.2 $O_2$ adsorption on supported $Cu_n$ Clusters .....	160
4.2.3 $O_2$ dissociation on supported $Cu_n$ Clusters.....	166
4.2.4 Successive dissociation of multiple $O_2$ molecules on supported $Cu_n$ clusters .....	171
4.2.4.1 $Cu_5$ clusters.....	171
4.2.4.2 $Cu_7$ clusters.....	177
4.3 $CH_4$ activation over $Cu_5$ -CHA-2Al clusters .....	184
4.4 Competing Processes in $Cu_5$ clusters .....	193
4.5 $CH_4$ activation over $Cu_7$ -CHA-2Al clusters .....	200
4.6 Competing processes in $Cu_7$ clusters.....	208
4.7 Discussion of the selective oxidation of methane into methanol over $Cu_n$ -2Al-CHA.....	213
4.8 Conclusions .....	220
4.9 Appendix .....	222
<b>Chapter 5 Alternative Zeotype Systems for the selective partial oxidation of methane into methanol.....</b>	<b>231</b>
5.1 Introduction .....	232
5.2 $O_2$ dissociation over $Cu_5$ -zeotype clusters.....	234
5.2.1 AlPO & SAPO systems.....	234
5.2.2 MeAPO systems .....	239
5.3 $CH_4$ activation over $Cu_5$ -2O zeotype systems .....	246
5.3.1 SAPO system.....	246
5.3.2 ZnAPO System.....	249
5.3.3 FeAPO System .....	251

5.3.4 MgAPO System.....	253
5.3.5 TiAPO System.....	255
5.3.6 ZrAPO System .....	257
5.3.7 SnAPO System.....	259
5.3.8 Brief discussion of the CH <sub>4</sub> activation on Cu <sub>5</sub> -2O-zeotype systems .....	261
5.4 Successive dissociation of O <sub>2</sub> molecules over Cu <sub>5</sub> -TiAPO systems .....	263
5.5 CH <sub>4</sub> activation over Cu <sub>5</sub> -3O TiAPO systems.....	267
5.6 Competitive Processes on Cu <sub>5</sub> -2O TiAPO system.....	270
5.7 Conclusions .....	272
5.8 Appendix .....	274
<b>Chapter 6 Conclusions</b> .....	<b>279</b>
<b>Summary</b> .....	<b>285</b>
<b>Resumen</b> .....	<b>291</b>
<b>Resum</b> .....	<b>297</b>
<b>List of Publications</b> .....	<b>303</b>
<b>References</b> .....	<b>305</b>