

TABLE OF CONTENTS

	Page
TABLE OF CONTENTS.....	i
LIST OF TABLES.....	ii
LIST OF FIGURES.....	iv
LIST OF ABBREVIATIONS.....	viii
INTRODUCTION.....	1
LITERATURE REVIEW.....	6
MATERIALS AND METHODS.....	11
Density Functional Theory.....	11
ONIOM Method.....	14
ONIOM energy.....	14
Treatment of link atoms.....	15
ONIOM gradients.....	18
(UFF) Universal Force Field.....	18
Details of Calculations.....	20
RESULTS AND DISCUSSION.....	25
Part I. Adsorption of H ₂ O ₂ on the Ti- substituted active site.....	25
Part II. Oxidative active site formation.....	32
Part III. Stability of oxidative active species.....	37
Part IV Epoxidation of unsaturated hydrocarbons.....	49
CONCLUSION.....	65
LITERATURE CITED.....	67

LIST OF TABLES

Table	Page
1 Selected optimized structural parameters of TS-1 active site models using the 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) scheme and the 9T B3LYP/6-31G(d,p) cluster.....	23
2 Selected optimized geometrical parameters of the adsorption complex (Ads_1), transition states (ts_1 and ts_2), and Int_4 using the 9T B3LYP/6-31G(d,p) cluster and the 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) scheme.....	30
3 Relative energies (kcal/mol) with respect to the isolated TS-1 model and H ₂ O ₂ gas of the adsorption complex (Ads_1), activation energies of ts_1 and ts_2 transition states, and oxidative active species of TS-1 calculated at the 30T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) method and at the 9T B3LYP/6-31G(d,p) cluster approach. The values in parentheses are the activation energies with respect to the Ads_1 complex.....	39
4 Selected optimized geometrical parameters of oxidative active species generated along the creation of oxidative active site using the 9T B3LYP/6-31G(d,p) cluster and the 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) scheme. Geometries are shown in Figures 5-7.....	40
5 Selected optimized geometrical parameters of the oxidative active species (Int_4), ethylene epoxidation transition states (ts_EO), and adsorption complex of TS-1/ethylene oxide (Ads_EO) using the 9T B3LYP/6-31G(d,p) cluster and the 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) scheme. Energies are the single point calculations of the optimized 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) structures using the 30T/65T ONIOM2 scheme. E_{app} is the apparent energies with respect to the isolated reactants and E_a is activation energy with respect to the Int_4 complex.....	53

LIST OF TABLES (Cont'd)

Table	Page
<p>6 Selected optimized geometrical parameters of the oxidative active species (Int_4), ethylene epoxidation transition states (ts_EO), and adsorption complex of TS-1/ethylene oxide (Ads_EO) using the 9T B3LYP/6-31G(d,p) cluster and the 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) scheme. Energies are the single point calculations of the optimized 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) structures using the 30T/65T ONIOM2 scheme. E_{app} is the apparent energies with respect to the isolated reactants and E_a is activation energy with respect to the Int_4 complex.....</p>	62
<p>7 Selected optimized geometrical parameters of the oxidative active species (Int_4), <i>trans</i>-2-butylene epoxidation transition states (ts_BO), and adsorption complex of TS-1/<i>trans</i>-2-butylene oxide (Ads_BO) using the 9T B3LYP/6-31G(d,p) cluster and the 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) scheme. Energies are the single point calculations of the optimized 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) structures using the 30T/65T ONIOM2 scheme. E_{app} is the apparent energies with respect to the isolated reactants and E_a is activation energy with respect to the Int_4 complex.....</p>	63

LIST OF FIGURES

Figure	Page
1 Proposed oxidative active species in the catalytic epoxidation reaction of unsaturated hydrocarbons with H_2O_2 over TS-1. The arrow represents the coordinative interaction.....	2
2 Schematic representation of the two-layered ONIOM extrapolation scheme.....	15
3 Definition of different atom within the ONIOM scheme.....	17
4 Showing (a) two tetrahedral sites (T5 and T6) of nondefect active site and optimized structures of defect active site models using (b) the 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) scheme and (c) the 9T B3LYP/6-31G(d,p) cluster. The high level region is displayed with balls and sticks whereas the low level region is demonstrated by lines.....	24
5 Showing the optimized structures of adsorption complex (Ads_1) of TS-1 and H_2O_2 calculated at the 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) method.....	27
6 Showing (a) the optimized structures of adsorption complex (Ads_1) of TS-1 and H_2O_2 calculated at the 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) method and (b) at the 9T B3LYP/6-31G(d,p) cluster. Some of the quantum region (balls and sticks) and the rest UFF region (lines) are omitted for clarity.....	28
7 Showing distorted octahedral conformation of adsorption complex (Ads_1) by close-up Figure 5. Some of the quantum region (balls and sticks) and the rest UFF region (lines) are omitted for clarity.....	29

LIST OF FIGURES (Cont'd)

Figure	Page
8 Showing optimized geometrical structures of the single proton mechanisms using the 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF).....	34
9 Showing optimized geometrical structures of the double proton mechanisms using the 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF).....	35
10 Optimized geometrical structures of (a)-(b) the single proton transfer and (c)-(d) the double proton transfer mechanisms using the 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) scheme and the 9T B3LYP/6-31G(d,p) cluster.....	36
11 Showing optimized geometrical structures of Ti-hydroperoxo complexes of Int_1 calculated at the 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) level of theory	42
12 Showing optimized geometrical structures of Ti-hydroperoxo complexes of Int_2 calculated at the 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) level of theory.....	43
13 Showing optimized geometrical structures of Ti-hydroperoxo complexes of Int_3 calculated at the 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) level of theory.....	44
14 Showing optimized geometrical structures of Ti-hydroperoxo complexes of Int_4 calculated at the 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) level of theory.....	45
15 Optimized geometrical structures of Ti-hydroperoxo complexes in different conformations calculated at the 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) level of theory. The conformations obtained from the 9T B3LYP/6-31G(d,p) cluster calculations are very similar to the ONIOM2 results, and thus are omitted.....	46
16 Showing distorted octahedral conformation of adsorption complex (Int_1) by close-up Figure 11. Some of the quantum region (balls and sticks) and the rest UFF region (lines) are omitted for clarity.....	47

LIST OF FIGURES (Cont'd)

Figure	Page
17 Showing optimized geometrical structures of Ti-hydroperoxo complexes of Int_5 calculated at the 9T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) level of theory.....	48
18 Showing optimized transition state structures of the ethylene epoxidation located at the cross section channel calculated at the ONIOM2(B3LYP/6-31G(d,p):UFF) level of theory.....	54
19 Showing optimized transition state structures of the ethylene epoxidation located at the straight channel calculated at the ONIOM2(B3LYP/6-31G(d,p):UFF) level of theory.....	55
20 Comparision of optimized transition state structures of the ethylene epoxidation located at (a) the cross section and (b) the straight channel. All optimized parameters are obtained from the energy minimization at the ONIOM2(B3LYP/6-31G(d,p):UFF) level of theory. Some parts of the quantum region (balls and sticks) and of MM region (lines) are omitted for clarity. The conformations obtained from the 9T B3LYP/6-31G(d,p) cluster are similar to the ONIOM2 results, and thus are omitted.....	56
21 Schematic energy profile of the overall epoxidation reaction of ethylene, propylene, and trans-2-butylene with H ₂ O ₂ over TS-1 calculated at the ONIOM2(B3LYP/6-31G(d,p):UFF) using the 30T/65T ONIOM cluster scheme.....	57
22 Showing optimized transition state structures of the propylene epoxidation located at the cross section channel calculated at the ONIOM2(B3LYP/6-31G(d,p):UFF) level of theory.....	59
23 Showing optimized transition state structures of the <i>trans</i> -2-butylene epoxidation located at the cross section channel calculated at the ONIOM2(B3LYP/6-31G(d,p):UFF) level of theory.....	60

LIST OF FIGURES (Cont'd)

Figure	Page
24 Comparison of optimized transition state complexes of (a) propylene and (b) <i>trans</i> -2-butylene epoxidation with H ₂ O ₂ over TS-1 calculated at the ONIOM2(B3LYP/6-31G(d,p):UFF) method level of theory. The conformations obtained from the 9T B3LYP/6-31G(d,p) cluster are similar to the ONIOM2 results, and thus are omitted.....	61
25 Optimized gas phase transition state complexes of (a) ethylene (b) propylene, and (c) <i>trans</i> -2-butylene epoxidation with H ₂ O ₂ calculated at the B3LYP/6-31G(d,p) level of theory.....	64

LIST OF ABBREVIATIONS

B3LYP	=	Becke's three parameter hybrid functional using the LYP correlation functional
BLYP	=	Beck-Lee-Yang-Parr functional
EXAFS	=	Extended X-ray Adsorption Fine Structure
DFT	=	Density Functional Theory
K	=	kelvin
kcal/mol	=	kilocalorie per mol
LANL2DZ	=	Los Alamos National Laboratory 2-Double-Zeta
LDA	=	Local Density Approximation
LSD	=	Local Spin Density approximation
MAS NMR	=	Magic Angle Spinning Nuclear Magnetic Resonance
MFI	=	Mobile Five framework type code
MM	=	Molecular Mechanics
MO	=	Molecular Orbital
ONIOM	=	Our own N-layered Integrated molecular Orbital and molecular Mechanics
ONIOM2	=	Our own two-layered Integrated molecular Orbital and molecular Mechanics
PND	=	Powder Neutron Diffraction
QM	=	Quantum Mechanics
QM/MM	=	Quantum Mechanics/Molecular Mechanics
SCF	=	Self-Consistent Field
SCREEP	=	Surface Charge Representation of External Embedded Potential Method

LIST OF ABBREVIATIONS (Cont'd)

STO-3G	=	Slater Type Orbital approximated by 3 Gaussian type orbitals
TMP	=	Trimethyl Phosphene
TS-1	=	Titanium Silicalite-1
UFF	=	Universal Force Field
VDW	=	van der Waals
XRD	=	X-ray Diffraction
ZSM-5	=	Zeolite Socony Mobil 5