

TABLE OF CONTENTS

	Page
TABLE OF CONTENTS.....	i
LIST OF TABLES.....	iii
LIST OF FIGURES.....	vii
ABBREVIATIONS.....	xii
INTRODUCTION.....	1
LITERATURE REVIEW.....	6
METHODS OF CALCULATIONS.....	10
Density functional theory (DFT).....	10
SCREEP method	
(The Surface Charge Represent of the Electrostatic Embedding	
Potential).....	13
Models and methodologies.....	15
ZSM-5 system.....	15
FAU system.....	16
RESULTS AND DISCUSSION.....	18
Mechanism of Beckmann rearrangement in zeolite catalyst.....	18
Brønsted acidic site of ZSM-5 zeolite.....	18
Adsorption complexes of formaldehyde oxime.....	19
Mechanism of the Beckmann rearrangement.....	23
Discussion.....	34
The influence of the framework to structures and energetic profiles	
of the vapor phase of the Beckmann rearrangement on different	
types of zeolite.....	36
1,2 H shift step.....	36
Rearrangement step.....	37
Tautomerization step.....	39
Discussion.....	50

TABLE OF CONTENTS (cont'd)

	Page
Influence of the framework and substituted group effects to structures and energetic profiles.....	51
1,2 H shift step.....	51
Rearrangement step.....	56
Tautomerization step.....	60
Discussion.....	66
CONCLUSION.....	68
LITERATURE CITED.....	70
APPENDIX.....	83

LIST OF TABLES

Table		Page
1	Zeolite structures and dimensional parameters.....	3
2	Optimized geometries and adsorption energy, ΔE_{ads} (in kcal/mol) for N-complexes and O-complexes in the bare clusters and embedded cluster at B3LYP/6-31G(d,p) level of theory. (Distances are in pm. and angles in degrees.).....	22
3	Optimized geometries and adsorption energy, ΔE_{ads} (in kcal/mol) for 1,2 H-shift transition state in the 10T bare cluster and embedded cluster at B3LYP/6-31G(d,p) level of theory. (Distances are in pm. and angles in degrees.).....	24
4	Optimized geometries and adsorption energy, ΔE_{ads} (in kcal/mol) for rearrangement step in the 10T bare cluster and embedded cluster at B3LYP/6-31G(d,p) level of theory. (Distances are in pm. and angles in degrees.).....	25
5	Optimized geometries and adsorption energy, ΔE_{ads} (in kcal/mol) for tautomerization step in the 10T bare cluster and embedded cluster at B3LYP/6-31G(d,p) level of theory. (Distances are in pm. and angles in degrees.).....	26
6	Comparison of the adsorption energy, ΔE_{ads} (in kcal/mol) along the Beckmann rearrangement of formaldehyde oxime on the 10T H-ZSM-5 zeolite in bare cluster and embedded cluster models by different methods. The values in square parentheses are obtained by the bare cluster model.....	27
7	Optimized geometries and adsorption energy, ΔE_{ads} (in kcal/mol) N-bound, 1,2 H-shift and O-bound complexes of formaldehyde oxime on the 12T bare cluster and embedded cluster at the B3LYP level of theory. The values in square parentheses are taken from the bare cluster model. (Distances are in pm. and angles in degrees.).....	41

LIST OF TABLES (cont'd)

Table	Page
<p>8 Optimized geometries and adsorption energy, ΔE_{ads} (in kcal/mol) rearrangement transition state and enol-amide complexes of formaldehyde oxime on the 12T bare cluster and embedded cluster at the B3LYP level of theory. The values in square parentheses are taken from the bare cluster model. (Distances are in pm. and angles in degrees.).....</p>	42
<p>9 Optimized geometries and adsorption energy, ΔE_{ads} (in kcal/mol) rearrangement transition state and keto-amide complexes of formaldehyde oxime on the 12T bare cluster and embedded cluster at the B3LYP level of theory. The values in square parentheses are taken from the bare cluster model. (Distances are in pm. and angles in degrees.).....</p>	43
<p>10 Comparison of the adsorption energy, ΔE_{ads} (in kcal/mol) along the Beckmann rearrangement of formaldehyde oxime on the 12T H-FAU zeolite in the bare cluster and embedded cluster models by different methods. The values in square parentheses are taken from the bare cluster model.....</p>	44
<p>11 Calculated proton affinities, PA (in kcal/mol) of corresponding amides of methylated derivatives at MP4/6-311G(d,p)/MP2/6-31G(d,p) level of theory.....</p>	61
Appendix Table	
<p>1 Optimized geometries of N-bound, 1,2 H-shift and O-bound complexes of Z-acetaldehyde oxime on the 12T bare cluster and embedded cluster at the B3LYP level of theory. The values in square parentheses are taken from the bare cluster model. (Distances are in pm. and angles in degrees.).....</p>	98

LIST OF TABLES (cont'd)

Appendix Table	Page
2 Optimized geometries of rearrangement transition state and enol-amide complexes of Z-acetaldehyde oxime on the 12T bare cluster and embedded cluster at the B3LYP level of theory. The values in square parentheses are taken from the bare cluster model. (Distances are in pm. and angles in degrees.).....	99
3 Optimized geometries of tautomerization transition state and keto-amide complexes of Z-acetaldehyde oxime on the 12T bare cluster and embedded cluster at the B3LYP level of theory. The values in square parentheses are taken from the bare cluster model. (Distances are in pm. and angles in degrees.).....	100
4 Optimized geometries of N-bound, 1,2 H-shift and O-bound complexes of E-acetaldehyde oxime on the 12T bare cluster and embedded cluster at the B3LYP level of theory. The values in square parentheses are taken from the bare cluster model. (Distances are in pm. and angles in degrees.).....	101
5 Optimized geometries of rearrangement transition state and enol-amide complexes of E-acetaldehyde oxime on the 12T bare cluster and embedded cluster at the B3LYP level of theory. The values in square parentheses are taken from the bare cluster model. (Distances are in pm. and angles in degrees.).....	102
6 Optimized geometries of tautomerization transition state and keto-amide complexes of E-acetaldehyde oxime on the 12T bare cluster and embedded cluster at the B3LYP level of theory. The values in square parentheses are taken from the bare cluster model. (Distances are in pm. and angles in degrees.).....	103

LIST OF TABLES (cont'd)

Appendix Table	Page
7 Optimized geometries of N-bound, 1,2 H-shift and O-bound complexes of acetone oxime on the 12T bare cluster and embedded cluster at the B3LYP level of theory. The values in square parentheses are taken from the bare cluster model. (Distances are in pm. and angles in degrees.).....	104
8 Optimized geometries of rearrangement transition state and enol-amide complexes of acetone oxime on the 12T bare cluster and embedded cluster at the B3LYP level of theory. The values in square parentheses are taken from the bare cluster model. (Distances are in pm. and angles in degrees.).....	105
9 Optimized geometries of tautomerization transition state and keto-amide complexes of acetone oxime on the 12T bare cluster and embedded cluster at the B3LYP level of theory. The values in square parentheses are taken from the bare cluster model. (Distances are in pm. and angles in degrees.).....	106

LIST OF FIGURES

Figure		Page
1	The illustrative models used in ab initio calculation: (a) the bare cluster model representing the active region of H-ZSM-5 zeolite, (b) the embedded cluster model which is imitation of the electrostatic potential from zeolite framework by point charges which surround on the bare cluster model and (c) the periodic model of H-ZSM-5, where the highlighted box is a supercell which is used in the periodic calculation.....	4
2	The embedded cluster models created from SCREEP approach.....	15
3	Presentation of the 10T bare cluster model of H-ZSM-5 zeolite.....	16
4	Presentation of the 12T bare cluster model of H-FAU zeolite.....	17
5	Optimized structures of 10T cluster and embedded cluster of H-ZSM-5 zeolite at B3LYP/6-31G(d,p) level of theory. (The values in parentheses are taken from the bare cluster.).....	18
6	Optimized adsorption complexes on the 10T cluster and embedded cluster of H-ZSM-5 zeolite at B3LYP/6-31G(d,p) level of theory. (a) N-bound complexes. (b) O-bound complexes (The values in parentheses are taken from the bare cluster.).....	21
7	Optimized complexes on 10T H-ZSM-5 zeolite at B3LYP/6-31G(d,p) level of theory. (a) 1,2 H-shift transition state complexes. (b) Beckmann rearrangement transition state complexes. (The values in parentheses are taken from the bare cluster.).....	28
8	Optimized complexes on 10T H-ZSM-5 zeolite at B3LYP/6-31G(d,p) level of theory. (a) enol-amide acid complexes. (b) tautomerization transition state complexes. (The values in parentheses are taken from the bare cluster.).....	29

LIST OF FIGURES (cont'd)

Figure		Page
9	Optimized the keto-amide complex on 10T H-ZSM-5 zeolite at B3LYP/6-31G(d,p) level of theory. (The values in parentheses are taken from the bare cluster.).....	30
10	Energetic profile along the pathway Beckmann rearrangement of formaldehyde oxime adsorbed on 10T H-ZSM-5 zeolite at MP2/6-311G(d,p)//B3LYP level of theory. The energetic changes for the embedded cluster (solid line) and the bare cluster (dash line) complexes are in kcal/mol.....	33
11	Optimized complexes on the 12T FAU zeolite at B3LYP/6-31G(d,p) level of theory. (a) N-bound complex. (b) 1,2 H-shift transition state complexes. (The values in parentheses are taken from the bare cluster.).....	45
12	Optimized complexes on the 12T FAU zeolite at B3LYP/6-31G(d,p) level of theory. (a) O-bound complex. (b) Beckmann rearrangement transition state complexes. (The values in parentheses are taken from the bare cluster.).....	46
13	Optimized complexes on the 12T FAU zeolite at B3LYP/6-31G(d,p) level of theory. (a) Enol-Amide complexes. (b) tautomerization transition state complexes. (The values in parentheses are taken from the bare cluster.).....	47
14	Optimized enol-amide complex on the 12T H-FAU zeolite at B3LYP/6-31G(d,p) level of theory. (The values in parentheses are taken from the bare cluster.).....	48

LIST OF FIGURES (cont'd)

Figure		Page
15	Energetic profile along the pathway Beckmann rearrangement of formaldehyde oxime adsorbed on the 12T H-FAU zeolite at MP2/6-311G(d,p)//B3LYP level of theory. The energetic changes for the embedded cluster (solid line) and the bare cluster (dash line) complexes are in kcal/mol.....	49
16	Energetic profile along the pathway Beckmann rearrangement of formaldehyde oxime adsorbed on zeolites at MP2/6-311G(d,p) //B3LYP level of theory. The energetic changes for the embedded cluster model of 10T of H-ZSM-5 zeolite (solid line) and the embedded cluster model of 12T of H-FAU zeolite (dot line) complexes are in kcal/mol.....	49
17	Optimized geometrical parameters of the corresponding N-bound complexes of (a) $H_2C=NOH$, (b) $Z-MeHC=NOH$, (c) $E-MeHC=NOH$, and (d) $Me_2C=NOH$ molecules on the 12T cluster and embedded cluster of H-FAU zeolite at the B3LYP/6-31G(d,p) level of theory.....	53
18	Optimized geometrical parameters of the corresponding O-bound complexes of (a) $H_2C=NOH$, (b) $Z-MeHC=NOH$, (c) $E-MeHC=NOH$, and (d) $Me_2C=NOH$ molecules on the 12T cluster and embedded cluster of H-FAU zeolite at the B3LYP/6-31G(d,p) level of theory.....	54
19	Optimized geometrical parameters of the corresponding 1,2 H-shift transition state structure of (a) $H_2C=NOH$, (b) $Z-MeHC=NOH$, (c) $E-MeHC=NOH$, and (d) $Me_2C=NOH$ molecules on the 12T cluster and embedded cluster of H-FAU zeolite at the B3LYP/6-31G(d,p) level of theory.....	55

LIST OF FIGURES (cont'd)

Figure		Page
20	Optimized geometrical parameters of the corresponding rearrangement transition state structure of (a) $\text{H}_2\text{C}=\text{NOH}$, (b) Z-MeHC=NOH, (c) E-MeHC=NOH, and (d) $\text{Me}_2\text{C}=\text{NOH}$ molecules on the 12T cluster and embedded cluster of H-FAU zeolite at the B3LYP/6-31G(d,p) level of theory.....	58
21	Optimized geometrical parameters of the corresponding enol-P complex of (a) $\text{H}_2\text{C}=\text{NOH}$, (b) Z-MeHC=NOH, (c) E-MeHC=NOH, and (d) $\text{Me}_2\text{C}=\text{NOH}$ molecules on the 12T cluster and embedded cluster of H-FAU zeolite at the B3LYP/6-31G(d,p) level of theory...	59
22	Optimized geometrical parameters of the corresponding tautomerization transition state structure complex of (a) $\text{H}_2\text{C}=\text{NOH}$, (b) Z-MeHC=NOH, (c) E-MeHC=NOH, and (d) $\text{Me}_2\text{C}=\text{NOH}$ molecules on the 12T cluster and embedded cluster of H-FAU zeolite at the B3LYP/6-31G(d,p) level of theory.....	62
23	Optimized geometrical parameters of the corresponding keto-P complex of (a) $\text{H}_2\text{C}=\text{NOH}$, (b) Z-MeHC=NOH, (c) E-MeHC=NOH, and (d) $\text{Me}_2\text{C}=\text{NOH}$ molecules on the 12T cluster and embedded cluster of H-FAU zeolite at the B3LYP/6-31G(d,p) level of theory...	63
24	Energetic profile along the pathway Beckmann rearrangement of four oxime molecules on 12T H-FAU zeolite at the MP2/6-311G(d,p)//B3LYP level of theory: (a) $\text{H}_2\text{C}=\text{NOH}$, (b) Z-MeHC=NOH systems, respectively. The energetic changes for the embedded cluster (solid line) and the bare cluster (dash line) complexes are in kcal/mol.....	64

LIST OF FIGURES (cont'd)

Figure		Page
25	Energetic profile along the pathway Beckmann rearrangement of four oxime molecules on 12T H-FAU zeolite at the MP2/6-311G(d,p)//B3LYP level of theory: (a) E-MeHC=NOH, and (b) Me ₂ C=NOH systems, respectively. The energetic changes for the embedded cluster (solid line) and the bare cluster (dash line) complexes are in kcal/mol. dash line) complexes are in kcal/mol.....	65
26	Schematic energy profiles of Beckmann rearrangement on the 12T embedded cluster model of FAU zeolite showing 1,2 H-shift, rearrangement and tautomerization steps of methylated derivatives. Values at the MP2/6-311G(d,p) //B3LYP level of theory. The energetic changes are in kcal/mol.....	66
Appendix Figure		
1	Methodology for creating charges represented zeolite framework by SCREEP method.....	84

LIST OF ABBREVIATION

B3LYP	=	Becke's three parameter hybrid functional using the LYP correlation functional
BR	=	Beckmann rearrangement
DFT	=	Density functional theory
FAU	=	Faujasite
FT-IR	=	Fourier Transform Infrared spectroscopy
GGA	=	Generalized gradient approximation
HF	=	Hartree Fock
H-ZSM-5	=	Proton-exchanged zeolite ZSM-5
H-FAU	=	Proton-exchanged zeolite FAU
LDA	=	Local density approximation
MAS-NMR	=	Magic-angle spinning Nuclear Magnetic Resonance
MP2	=	The second order Møller-Plesset perturbation theory
MOR	=	Mordenite
NMR	=	Nuclear Magnetic Resonance
SCREEP	=	Surface Charge Representation of the Electrostatic Embedding Potential
T	=	Tetrahedral
ZSM-5	=	Zeolite Scony Mobile-structure 5
6-31G(d,p)	=	Pople valence double zeta plus d and p polarization functions for heavy atom and hydrogen atoms
6-311G(d,p)	=	Pople valence triple zeta plus d and p polarization functions for heavy atom and hydrogen atoms