

**ADSORPTION OF *m*- AND *p*-CHLORONITROBENZENE ON  
FAUJASITE ZEOLITES AND ITS APPLICATION ON  
CRYSTALLIZATION**



Benyapa Yensukjit

A Thesis Submitted in Partial Fulfilment of the Requirements  
for the Degree of Master of Science  
The Petroleum and Petrochemical College, Chulalongkorn University  
in Academic Partnership with  
The University of Michigan, The University of Oklahoma,  
Case Western Reserve University, and Institute Francais du Petrole  
2009

522067

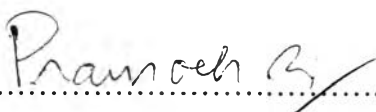
**Thesis Title:** Adsorption of *m*- and *p*-Chloronitrobenzene on FAU Zeolites and Its Application on Crystallization  
**By:** Benyapa Yensukjit  
**Program:** Petrochemical Technology  
**Thesis Advisors:** Assoc. Prof. Pramoch Rangsunvigit  
Dr.Santi Kulprathipanja

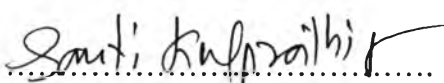
---

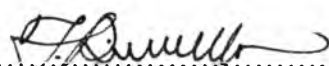
Accepted by The Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.


  
..... College Dean  
(Asst. Prof. Pomthong Malakul)

**Thesis Committee:**

  
.....  
(Assoc. Prof. Pramoch Rangsunvigit)

  
.....  
(Dr. Santi Kulprathipanja)

  
.....  
(Assoc. Prof. Thirasak Rirksomboon)

  
.....  
(Assoc. Prof. Paisan Kongkachuichay)

## ABSTRACT

5071006063: Petrochemical Technology Program

Benyapa Yensukjit: Adsorption of *m*- and  
*p*-Chloronitrobenzene on FAU Zeolites and Its Application on  
Crystallization

Thesis Advisors: Assoc. Prof. Pramoch Rangsunvigit, Dr. Santi  
Kulprathipanja 61 pp.

Keywords: Adsorption/ Crystallization/ Chloronitrobenzene/ Zeolite/ Separation

Adsorption isotherms of *m*- and *p*-chloronitrobenzene (CNB), isomeric substances on FAU zeolites with alkaline earth exchanged cations were studied under static conditions at 30°C. The experiment was carried out by preparing 1 to 8 wt% of *m*- and *p*-CNB in the solution. Hexane and dodecane were used as the solvent and tracer, respectively. The composition was determined by a gas chromatograph. The results further substantiated the adsorption behavior of CNBs on the FAU zeolites with the alkaline exchanged cations. The adsorption capacities of CNBs on both types of zeolite partly depended on the acid–base interaction. Normally, *m*-CNB was selectively adsorbed by the zeolites more than *p*-CNB due to a higher dipole moment or higher basicity. The adsorption capacities of *m*- and *p*-CNB on the zeolites with both the alkaline and the alkaline earth exchanged cations increased with the acid strength of the zeolite. NaY and CaY were the most appropriate adsorbent for CNBs separation because they offered the high adsorption capacity of CNBs and a high *m*-/*p*-CNB selectivity. Moreover, the FAU zeolites were also used in the crystallization of *m*- and *p*-CNB to study their effect on the precipitate composition.

## บทคัดย่อ

เบญญาภา เย็นสุขจิตต์: การศึกษาการแยกเมทา- และพารา-คลอโรไนโตรเบนซีนด้วยกระบวนการดูดซับด้วยซีโอไลต์และการประยุกต์ใช้ซีโอไลต์ในการตกผลึก (Adsorption of *m*- and *p*-chloronitrobenzene on FAU Zeolites and its Application on Crystallization) อ. ที่ปรึกษา: รศ. ดร. ปราโมช รังสรรค์วิจิตร และ ดร. สันติ กุลประทีปปัญญา 61 หน้า

การศึกษาระบบการดูดซับคลอโรไนโตรเบนซีนไอโซเมอร์ด้วยซีโอไลต์ที่แลกเปลี่ยนไอออนด้วยหมู่อัลคาไลน์เอิร์ธ ณ สภาวะสมดุลสถิต ที่ 30 องศาเซลเซียส ในกระบวนการทดลองใช้สารผสมเมทา- และพารา-คลอโรไนโตรเบนซีนที่ความเข้มข้นระหว่าง 1-8 เปอร์เซ็นต์ โดยน้ำหนักของสารละลาย โดยมีเฮกเซนและโคเคเคนเป็นตัวทำละลายและสารมาตรฐานตามลำดับในการหาค่าองค์ประกอบของสารละลายได้ใช้เทคนิคก๊าซโครมาโตกราฟและได้ทำการเปรียบเทียบผลการศึกษาดูดซับกับงานวิจัยการดูดซับคลอโรไนโตรเบนซีนไอโซเมอร์ด้วยซีโอไลต์ที่แลกเปลี่ยนไอออนด้วยหมู่อัลคาไลน์ จากผลการวิจัยทั้งสองพบว่าพฤติกรรมการดูดซับของคลอโรไนโตรเบนซีนไอโซเมอร์บนซีโอไลต์มีผลดังนี้ ค่าความจุการดูดซับของสารคลอโรไนโตรเบนซีนไอโซเมอร์ขึ้นอยู่กับความเป็นกรด-เบสของตัวดูดซับและตัวถูกดูดซับ โดยที่ซีโอไลต์ซึ่งเป็นตัวดูดซับเลือกดูดซับเมทา-คลอโรไนโตรเบนซีนมากกว่าพารา-คลอโรไนโตรเบนซีน เนื่องจากเมทา-คลอโรไนโตรเบนซีนมีความเป็นเบสมากกว่าหรือมีความสามารถในการให้อิเล็กตรอนได้มากกว่าพารา-คลอโรไนโตรเบนซีน ดังนั้นเมทา-คลอโรไนโตรเบนซีนจึงสามารถสร้างแรงยึดกับซีโอไลต์ได้ดีกว่าพารา-คลอโรไนโตรเบนซีน ค่าความจุการดูดซับของคลอโรไนโตรเบนซีนไอโซเมอร์บนซีโอไลต์เพิ่มขึ้นตามความเป็นกรดของซีโอไลต์ทั้งที่แลกเปลี่ยนไอออนด้วยหมู่อัลคาไลน์และอัลคาไลน์เอิร์ธ นอกจากนี้ยังได้ใช้ซีโอไลต์ในกระบวนการตกผลึกสารคลอโรไนโตรเบนซีนไอโซเมอร์ เพื่อศึกษาผลของซีโอไลต์ต่อค่าองค์ประกอบของผลึกคลอโรไนโตรเบนซีนที่ได้ด้วย

## ACKNOWLEDGEMENT

This thesis could not be completed without the assistance of many people and support of my advisor, co-advisor, college and my family.

First, I would like to express my gratitude to Dr. Santi Kulprathipanja, my co-advisor, for giving me the best opportunity of visiting UOP, A Honeywell Company in Chicago and spending two weeks with his family in US. Even it was a short time; I received a great valuable experience in my life. He taught me not only the way to work, to solve the problem, to work as a team, to balance between life and work, and also taught me to be a good person. Moreover, I am indebted to his wife, too, Mrs. Apinya Kulprathipanja, for her kindness. They took a very good care of me.

I also appreciate Assoc. Prof. Pramoch Rangsunvigit, my advisor. He provided superb guidance, encouragement, and creative suggestion. My thanks are also for his kindness, for being patient in listening to my opinion and in proofing my writing.

I am grateful for the full scholarship and partial funding of the thesis work provided by Center for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University.

Special thanks are extended to UOP, A Honeywell Company, for providing me a budget for observing research both in Thailand and in US. Also, I would like to thank the people who did favors for me during my visit there.

Finally, I would like to thank all of my friends for their friendly cheerful and useful assistance. Also, I would like to take this opportunity to thank my parents for their encouragement, understanding, and love.

## TABLE OF CONTENTS

	<b>PAGE</b>
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgement	v
Table of Contents	vi
List of Tables	viii
List of Figures	ix
<b>CHAPTER</b>	
<b>I INTRODUCTION</b>	<b>1</b>
<b>II LITERATURE REVIEW</b>	<b>3</b>
<b>III EXPERIMENTAL</b>	<b>19</b>
3.1 Materials	19
3.1.1 Chemicals	19
3.1.2 Adsorbents	19
3.1.3 Solvents	19
3.2 Equipment	20
3.3 Methodology	20
3.3.1 Static Adsorption Study of <i>m</i> - and <i>p</i> -CNB	20
3.3.1.1 Single Component Adsorption Study	20
3.3.1.2 Binary Component Adsorption Study	20
3.3.2 Effect of FAU Zeolite on Crystallization Study of <i>m</i> - and <i>p</i> -CNB	21
<b>IV RESULTS AND DISCUSSION</b>	<b>22</b>
4.1 Static Adsorption of <i>m</i> - and <i>p</i> -CNB	22
4.1.1 Single Component Adsorption	22

<b>CHAPTER</b>	<b>PAGE</b>
4.1.2 Binary Component Adsorption	36
4.2 Effect of FAU Zeolite on Crystallization of <i>m</i> - and <i>p</i> -CNB	48
4.2.1 Effect of FAU Zeolites on CNBs Mixture Composition	48
4.2.2 Effect of FAU Zeolites on the Precipitate Composition of <i>m</i> - and <i>p</i> -CNB	48
<b>V CONCLUSIONS AND RECOMMENDATIONS</b>	<b>55</b>
<b>REFERENCES</b>	<b>57</b>
<b>APPENDIX</b>	<b>60</b>
Appendix A Adsorption Capacities of <i>m</i> -CNB and <i>p</i> -CNB on the X and Y zeolites from the Single Component Systems, Equilibrium Constant (K) and Determination Coefficiency ( $R^2$ )	60
<b>CURRICULUM VITEA</b>	<b>61</b>

## LIST OF TABLES

TABLE	PAGE
2.1 Chemical properties of each CNB isomer	3
2.2 Enthalpies of crystallization and distillation	8
3.1 Chemical composition for various faujasite zeolite	19
4.1 Adsorption capacities of <i>m</i> - and <i>p</i> -CNB on FAU zeolite with the alkaline earth exchanged cations	31
4.2 Kinetic diameters and molecular dipole moments of <i>m</i> -CNB and <i>p</i> -CNB	32
4.3 <i>m</i> - and <i>p</i> -CNB composition in the original mixture and the mixture with 10 grains of the zeolites at 30°C	49
4.4 Composition of <i>m</i> - and <i>p</i> -CNB in the precipitates located near the zeolite or (a) area at 22°C	51
4.5 Composition of <i>m</i> - and <i>p</i> -CNB in the precipitates located far from the zeolite or (b) area at 22°C	52
4.6 Composition of <i>m</i> - and <i>p</i> -CNB in the mixture at the zeolite or (a) area and far from the zeolite or (b) area at 30 and 22°C	53
A1 Adsorption capacities of <i>m</i> -CNB, equilibrium constant (K) and determination coefficient ( $R^2$ )	60
A2 Adsorption capacities of <i>p</i> -CNB, equilibrium constant (K) and determination coefficient ( $R^2$ )	60



## LIST OF FIGURES

FIGURE	PAGE
2.1	Three isomers of CNBs. <span style="float: right;">3</span>
2.2	Binary solid-liquid phase diagrams encountered in melt crystallization. <span style="float: right;">9</span>
2.3	Phase diagram for the simple eutectic system naphthalene-benzene. <span style="float: right;">13</span>
2.4	Line representations of zeolite structure. <span style="float: right;">17</span>
3.1	Crystallization unit. <span style="float: right;">21</span>
4.1	Adsorption isotherm of <i>m</i> -CNB on MgX at 30°C. <span style="float: right;">22</span>
4.2	Adsorption isotherm of <i>p</i> -CNB on MgX at 30°C. <span style="float: right;">23</span>
4.3	Adsorption isotherm of <i>m</i> -CNB on CaX at 30°C. <span style="float: right;">23</span>
4.4	Adsorption isotherm of <i>p</i> -CNB on CaX at 30°C. <span style="float: right;">24</span>
4.5	Adsorption isotherm of <i>m</i> -CNB on SrX at 30°C. <span style="float: right;">24</span>
4.6	Adsorption Isotherm of <i>p</i> -CNB on SrX at 30°C. <span style="float: right;">25</span>
4.7	Adsorption isotherm of <i>m</i> -CNB on BaX at 30°C. <span style="float: right;">25</span>
4.8	Adsorption isotherm of <i>p</i> -CNB on BaX at 30°C. <span style="float: right;">26</span>
4.9	Adsorption isotherm of <i>m</i> -CNB on MgY at 30°C. <span style="float: right;">26</span>
4.10	Adsorption isotherm of <i>p</i> -CNB on MgY at 30°C. <span style="float: right;">27</span>
4.11	Adsorption isotherm of <i>m</i> -CNB on CaY at 30°C. <span style="float: right;">27</span>
4.12	Adsorption isotherm of <i>p</i> -CNB on CaY at 30°C. <span style="float: right;">28</span>
4.13	Adsorption isotherm of <i>m</i> -CNB on SrY at 30°C. <span style="float: right;">28</span>
4.14	Adsorption isotherm of <i>p</i> -CNB on SrY at 30°C. <span style="float: right;">29</span>
4.15	Adsorption isotherm of <i>m</i> -CNB on BaY at 30°C. <span style="float: right;">29</span>
4.16	Adsorption isotherm of <i>p</i> -CNB on BaY at 30°C. <span style="float: right;">30</span>
4.17	Relation of adsorption capacities of <i>m</i> - and <i>p</i> -CNB on the X and Y zeolites with alkaline earth exchanged cation and ionic radius. <span style="float: right;">32</span>

FIGURE	PAGE
4.18 Relation of adsorption capacities of <i>m</i> - and <i>p</i> -CNB on the X and Y zeolites with alkaline earth exchanged cation and Sanderson's intermediate electronegativity ( $S_{int}$ ).	34
4.19 Relation of adsorption capacities of <i>m</i> - and <i>p</i> -CNB on the series of X and Y zeolites with alkaline exchanged cation and ionic radius.	34
4.20 Relation of adsorption capacities of <i>m</i> - and <i>p</i> -CNB on the FAU zeolites with alkaline exchanged cation and Sanderson's intermediate electronegativity ( $S_{int}$ ).	35
4.21 Binary adsorption isotherms of <i>m</i> - and <i>p</i> -CNB on MgX at 30°C.	36
4.22 Binary adsorption isotherms of <i>m</i> - and <i>p</i> -CNB on CaX at 30°C.	36
4.23 Binary adsorption isotherms of <i>m</i> - and <i>p</i> -CNB on SrX at 30°C.	37
4.24 Binary adsorption isotherms of <i>m</i> - and <i>p</i> -CNB on BaX at 30°C.	37
4.25 Binary adsorption isotherms of <i>m</i> - and <i>p</i> -CNB on MgY at 30°C.	38
4.26 Binary adsorption isotherms of <i>m</i> - and <i>p</i> -CNB on CaY at 30°C.	38
4.27 Binary adsorption isotherms of <i>m</i> - and <i>p</i> -CNB on SrY at 30°C.	39
4.28 Binary adsorption isotherms of <i>m</i> - and <i>p</i> -CNB on BaY at 30°C.	39
4.29 Binary competitive adsorption and total adsorption capacity isotherms at 30°C on MgX.	41
4.30 Binary competitive adsorption and total adsorption capacity isotherms at 30°C on MgY.	41

FIGURE	PAGE
4.31 Adsorption capacities of <i>m</i> - and <i>p</i> -CNB, and total adsorption capacity for the binary competitive adsorption with acid strength of the X zeolites with alkaline earth exchanged cation.	42
4.32 Adsorption capacities of <i>m</i> - and <i>p</i> -CNB, and total adsorption capacity for the binary competitive adsorption with acid strength of the Y zeolites with alkaline earth exchanged cation.	42
4.33 Adsorption capacities of <i>m</i> - and <i>p</i> -CNB, and total adsorption capacity for the binary competitive adsorption with acid strength of the X zeolites with alkaline exchanged cation.	43
4.34 Adsorption capacities of <i>m</i> - and <i>p</i> -CNB, and total adsorption capacity for the binary competitive adsorption with acid strength of the Y zeolites with alkaline exchanged cation.	44
4.35 <i>m</i> -CNB/ <i>p</i> -CNB adsorption selectivity of the X zeolites with alkaline earth exchanged cation as function of Sanderson's intermediate electronegativity ( $S_{int}$ ).	45
4.36 <i>m</i> -CNB/ <i>p</i> -CNB adsorption selectivity of the Y zeolites with alkaline earth exchanged ion as function of Sanderson's intermediate electronegativity ( $S_{int}$ ).	45
4.37 <i>m</i> -CNB/ <i>p</i> -CNB selectivity as a function of equilibrium concentration in liquid phase on NaY zeolite	47
4.38 <i>m</i> -CNB/ <i>p</i> -CNB selectivity of the zeolites with alkaline exchanged cation at low (a and b) and high (c and d) equilibrium concentration as function of Sanderson's intermediate electronegativity ( $S_{int}$ ).	48
4.39 Binary phase diagram of <i>m</i> -CNB and <i>p</i> -CNB.	50
4.40 Locations where precipitates are taken for <i>m</i> - and <i>p</i> -CNB composition analysis.	51

<b>FIGURE</b>	<b>PAGE</b>
4.41 Crystallizer.	54