HYDROTHERMAL SYNTHESIS OF METAKAOLIN BASED ZEOLITE T WITH THREE DIFFERENT STRUCTURE DIRECTING AGENTS AND ITS ADSORPTION CAPACITY TOWARD CARBON DIOXIDE

SITI ZUBAIDAH PATUWAN

PERPUSTAKAAN
UNIVERSITI MALAYSIA SABAH

THESIS SUBMITTED IN FULFILLMENT FOR THE
DEGREE OF MASTER OF SCIENCE

FACULTY OF SCIENCE AND NATURAL RESOURCES
UNIVERSITI MALAYSIA SABAH
2018
UNIVERSITI MALAYSIA SABAH
BORANG PENGESAHAN STATUS TESIS

JUDUL: HYDROTHERMAL SYNTHESIS OF METAKAOLIN BASED ZEOLITE T WITH THREE DIFFERENT STRUCTURE DIRECTING AGENTS AND ITS ADSORPTION CAPACITY TOWARD CARBON DIOXIDE

IJAZAH: SARJANA SAINS (KIMIA INDUSTRI)

Saya SITI ZUBAIDAH BINTI PATUWAN sesi 2014-2017 mengaku membenarkan tesis Sarjana ini disimpan di Perpustakaan Universiti Malaysia Sabah dengan syarat-syarat kegunaan seperti berikut:-

1. Tesis ini adalah hak milik Universiti Malaysia Sabah.
2. Perpustakaan Universiti Malaysia Sabah dibenarkan membuat salinan untuk tujuan pengajian sahaja.
3. Perpustakaan dibenarkan membuat salinan tesis ini sebagai bahan pertukaran antara institusi pengajian tinggi.
4. Sila tandakan (/):
   - [ ] SULIT (Mengandungi maklumat yang berdjarah keselamatan atau kepentingan Malaysia seperti yang termaktub di dalam AKTA RAHSIA 1972)
   - [ ] TERHAD (Mengandungi maklumat terhad yang telah ditentukan oleh organisasi/badan di mana penyelidikan dijalankan)
   - [ ] TIDAK TERHAD

SITI ZUBAIDAH BINTI PATUWAN
MS1421117T

Tarikh: 01 Mar 2018

Disahkan Oleh,

NURULAIN BINTI ISMAIL
POSTAKAWAN KAJAN
UNIVERSITI MALAYSIA SABAH

(Tandatangan Pustakawan)

(Sir ZUBAIDAH BINTI PATUWAN
MS1421117T

Disahkan Oleh,

IN BINTI ISMAIL

Penyelia

(Prof. Madya Dr. Sazma Arshad)

Tandatangan Penyelia
DECLARATION

I hereby declare that the experimental work and results in this thesis entitled, "Hydrothermal Synthesis of Metakaolin Based Zeolite T with Three Different Structure Directing Agents and Its Adsorption Capacity toward Carbon Dioxide" is entirely authentic and was carried out by me independently under the guide and supervision of Assc. Prof. Dr. Sazmal E. Arshad, Associate Professor in Inorganic Chemistry, Faculty of Science and Natural Resources of Universiti Malaysia Sabah, Malaysia, and has not been included in any other thesis submitted previously for the award of any degree.

27TH NOVEMBER 2017

Siti Zubaidah Patuwan
MS1421117T
CERTIFICATION

NAME : SITI ZUBAIDAH BINTI PATUWAN
MATRIC NO : MS1421117T
TITLE : HYDROTHERMAL SYNTHESIS OF METAKAOLIN BASED ZEOLITE T WITH THREE DIFFERENT STRUCTURE DIRECTING AGENTS AND ITS ADSORPTION CAPACITY TOWARD CARBON DIOXIDE
DEGREE : MASTER OF SCIENCE (INDUSTRIAL CHEMISTRY)
VIVA DATE : 27TH NOVEMBER 2017

CERTIFIED BY

SUPERVISOR
ASSC. PROF. DR. SAZMAL EFFENDI ARSHAD

SIGNATURE

iii
ACKNOWLEDGMENT

Alhamdulillah. I wish to express my deep sense of gratitude to my supervising guide, Assc. Prof. Dr. Sazmal Effendi Arshad for his stimulating discussions and the constant help - both professional and personal - that he rendered throughout, without which this work would not have been submitted in its present form. I couldn’t be more happy to be his student, given the responsibilities with freedom.

I am deeply indebted to Prof. Taufiq Yap Yun Hin, Professor at Faculty of Science Catalysis, PUTRACAT of Universiti Putra Malaysia, for providing me with the necessary facility to carry out a part of my work there. I am grateful to Prof. Md. Lutfor Raman and Dr Shaheen Sarkar, for their help during the course of the study and providing me a facility at Universiti Malaysia Pahang.

I also deeply indebted to my friends, especially to Ms. Noorazwaziah Malik and Mr. Mahashanon Arumugam , scholars in catalysis at PUTRACAT, UPM, for their meticulous planning and scheduling for TPD at PUTRACAT and also for Mr. Tapan Biswas, for his timely guidance in utilizing the BET at UMP. My friends and colleagues- Repa, Ayu, Fina, Mon, Teri, Dadak, Shiva and Shallyne, who have stood by me through thick and thin, have been my major motivation and source of inspiration, all along.

I would be remiss in my duty if I fail to thank Mr. Eddy Farid Yuslee, Head of Project for this study and his scientific inputs during the course of the study, and for generously trusted me as a research assistant for grant of RAG-0068-SG-2015 provided by Universiti Malaysia Sabah. Also all the teaching and non-teaching staff of FSSA, PPST, IBTP, IPB and PPI for their help and supports behind the scenes.

To my mom and dad, my brothers and sister, who have patiently inspired me with their love, unfailing support, trust and encouragement – Terima Kasih! Kakak sayang kamu semua.

Last but not the least it would be ungracious of me not to mention the financial support from myBrain15 of Kementerian Pendidikan Tinggi Malaysia, and also the EKPP by Universiti Malaysia Sabah, which is greatly acknowledged.

Siti Zubaidah Patuwan

Responsible with Freedom

27th NOV 2018
ABSTRACT

Technology in carbon dioxide gas capture by synthetic zeolite material have been a breakthrough during last decades. However, many fundamental challenges in synthesis zeolite material and usually involves expensive reagents. Therefore, this work focuses in overcoming the present limitation in developing new synthesis concept for the synthesis and functionalization of zeolite T from metakaolin for carbon dioxide (CO₂) adsorption. The metakaolin (Si-Al source) was a commercialized kaolin powder that undergone temperature treatment at 750 °C for four hours, followed by the preparation of zeolite mixture. Zeolite T was synthesized hydrothermally by following the molar ratio of chemical components SiO₂:Al₂O₃:Na₂O:K₂O:H₂O (1:0.04:0.26:0.09:14), whereas the several reaction parameters, i.e synthesis temperature, reaction time, types of structure directing agents, SDA (TMOAH, TEAOH, and TBAOH) were studied. Furthermore, the pore properties and adsorption-desorption of zeolite T (correspond to different SDA) toward CO₂ were investigated. Zeolite T was prepared using TMAOH and XRD pattern obtained under different TMAOH ratio (0.05 – 0.25) shows a pure crystals of rice-like zeolite T and crystallized in nano-sizes at the highest ratio of 0.25. Meanwhile, the behavior of zeolite T crystals in TEAOH resulting a co-exist system between species of zeolite T and L under range ratios of 0.05, 0.10, 0.15, and 0.20, while the species of zeolite W was obtained at the highest TEAOH ratio (0.25). System with TBAOH as SDA have led the formation of acicular crystals with negative growth of zeolite T and unstable form of zeolite L crystals at ratio 0.10 and forming poor crystallization system at remaining ratios (0.05, 0.15, 0.20, and 0.25). The pure form of zeolite T prepared at lowest ratio of 0.05 TMAOH, possessed surface area and pore size of 357.9 m²/g and 24.96 Å respectively, shows an excellent adsorption-desorption by able to adsorbed 4893 µmol/g of CO₂ and fully desorbed at temperature 907 °C.
**ABSTRAK**

**SINTESES HIDRROTHERMA ZEOLITE T BERASASKAN METAKAOLIN DENGAN TIGA JENIS EJEN PENGGUSTRUKTURAN KHASUS DAN KAPASITI PENGERAPAN TERHADAP GAS KARBON DIOKSIDA**

Teknologi dalam menjerap gas karbon dioksida melalui bahan zeolit sintetik telah menjadi satu penemuan selama beberapa dekade yang lalu. Walau bagaimanapun, terdapat halangan dalam penyediaan bahan baru untuk sintesis zeolit dan biasanya melibatkan kos reagen yang tinggi. Oleh itu, penyelidikan ini memberi tumpuan untuk menyatukan batasan kajian dan mengembangkan teknologi baru di dalam bidang sintesis dan kegunaan zeolit T dari metaakaolin untuk penjerapan karbon dioksida (CO₂). Metaakaolin (sumber Si-Al) merupakan serbuk kaolin yang dikomersialkan dan telah menjalani rawatan suhu pada 750 °C selama empat jam, dan digunakan sebagai penyediaan campuran zeolit. Zeolite T disintesis secara hidrotermal dengan nisbah molar SiO₂: Al₂O₃: Na₂O: K₂O: H₂O (1: 0.04: 0.26: 0.09: 14), manakala beberapa parameter tindak balas seperti suhu, masa tindakbalas, jenis ejen pengstruktur an khusus, SDA (TMOAH, TEAOH, dan TBAOH) telah dikaji. Tambahannya pula, sifat-sifat poros dan penjerapan-penyahjarapan zeolit T (berdasarkan SDA yang berbeza) terhadap CO₂ telah dijalankan. Keputusan XRD untuk Zeolit T yang disediakan dengan TMAOH mengikuti nisbah yang berbeza (0.05 - 0.25) menunjukkan penghasilan hablur tulent zeolit T seperti beras dan saiz kristal adalah nanos pada nisbah maksima 0.25. Sementara itu, sifat penghabluran zeolit T dengan TEAOH menggunakan nisbah 0.05, 0.10, 0.15 dan 0.20 telah menghasilkan spesis zeolit T yang wujud bersama-sama dengan zeolit L di dalam satu sistem. Manakala spesis zeolit W diporeoleh pada nisbah maksima TEAOH (0.25). Sistem dengan TBAOH sebagai SDA telah menyebabkan pembentukan hablur jejarum yang tidak ketahu, serta penghabluran zeolit T yang negatif dan pembentukan hablur zeolit L yang tidak stabil pada nisbah 0.10. Ia juga memembentuk penghabluran yang lemah pada nisbah 0.05, 0.15, 0.20 dan 0.25. Zeolit T yang tuken dengan nisbah terendah 0.05 TMAOH mempunyai luas permukaan 357.9 m²/g dan saiz liang 24.96 Å, ia menunjukkan penjerapan-penyahjerapan yang unggul dengan menjerap CO₂ sebanyak 4893 µmol/g dan penyahjerapan sepenuhnya pada suhu 907 °C.
# LIST OF CONTENTS

<table>
<thead>
<tr>
<th>TITLE</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>DECLARATION</td>
<td>ii</td>
</tr>
<tr>
<td>CERTIFICATION</td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>iv</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>v</td>
</tr>
<tr>
<td>ABSTRAK</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF CONTENTS</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xii</td>
</tr>
<tr>
<td>LIST OF ABBREVIATION AND SYMBOLS</td>
<td>xvii</td>
</tr>
<tr>
<td>LIST OF APPENDICES</td>
<td>xix</td>
</tr>
</tbody>
</table>

## CHAPTER 1: INTRODUCTION

1.1 Study Background
1.2 Research Objectives
1.3 Problem Statements
1.4 Scope of Research

## CHAPTER 2: LITERATURE REVIEW

2.1 Zeolite T: First generation zeolites
2.2 Synthesis parameters of zeolite T
   2.2.1 Effect of Crystallization Temperature and Time
   2.2.2 Effect of Silica and Alumina Parameter
   2.2.3 Effect of pH and Water Ratio
   2.2.4 Effect of Structure Directing Agent
2.3 Co-exist species
   2.3.1 Zeolite L
   2.3.2 Zeolite W
2.4 Application of Zeolite T
   2.4.1 Adsorption Properties
   2.4.2 Pervaporation Properties
2.5 Clay for Alumino-silicate Source
   2.5.1 Kaolinite
   2.5.2 Metakaolin
2.6 Characterization Technology for Zeolite T
   2.6.1 X-ray Diffraction
LIST OF TABLES

Table 2.1 Different zeolite phase obtained from varied crystallization conditions (Mirfendereski & Mohammadi, 2011).

Table 2.2 The Si/Al molar ratio and silica source with resulting product phases obtained from study conducted by Rad et al. (2012).

Table 2.3 Different types of silica and alumina sources with correspond researchers.

Table 2.4 Optimum condition on synthesizing zeolite L, W and T under same composition mixture (Mirfendereski & Mohammadi, 2010).

Table 2.5 The textural properties and isothermal adsorption of zeolite T obtained by using BET analyzer (Jiang et al., 2013).

Table 2.6 The breakthrough time for zeolite T for dynamic adsorption performance (Jiang et al., 2013).

Table 2.7 The comparison of PV performance of different zeolite membranes with respect of different references (Cui et al., 2004; Zhou et al., 2013).

Table 2.8 The representative physical constant of kaolinite.

Table 2.9 The physical and chemical characteristics of common kaolinite.

Table 2.10 The values of 2θ and relative intensity (I, %) for characterization peaks of zeolite T, L and W (Treacy & Higgins, 2001; Mirfendereski & Mohammadi, 2011).

Table 3.1 The composition and parameters of free-template samples synthesized.

Table 3.2 Composition of samples synthesized by using different SDA at 100°C, 168 h.

Table 4.1 The phase evolutions of zeolites crystals with respect of crystallization time and temperature.

Table 4.2 The summary of different crystals level formed in different types of SDA and its respective ranges.
Table 4.3  Information on chemical composition and types of zeolite obtained for seven selected samples.

Table 4.4  BET texture adsorption data of zeolite T with different ratio of SDAs.

Table 4.5  Desorption phase of carbon dioxide gas by zeolite T with different SDA.
| Figure 2.1 | Hexagonal crystal structure of (a) offretite and (b) erionite (Mougenel & Kessler, 1991) | Page 6 |
| Figure 2.2 | Structural framework of erionite, viewed normal to [100]. | 6 |
| Figure 2.3 | Structural framework of offretite, viewed normal to [001] | 7 |
| Figure 2.4 | Framework of zeolite T (a) [001] perpendicular view and height of cancrinite cage of zeolite T and (b) [100] parallel view of stacking layers of offretite and erionite respectively (Holmes, 2011; Jusoh et al., 2017). | 8 |
| Figure 2.5 | Morphologies of zeolite T (a) FESEM & (b) high magnified SEM (Yeo et al., 2014), (c) SEM (Wang et al., 2014), (d) SEM (Zhou et al., 2013). | 9 |
| Figure 2.6 | The XRD peaks of samples prepared at 120 h at different temperature of 100 °C, 120 °C and 140 °C. (Source: Mirfenderski and Mohammadi, 2011). | 12 |
| Figure 2.7 | The XRD patterns of zeolite T synthesized at different time. (Source: Zhou et al., 2009) | 13 |
| Figure 2.8 | (a), (b) the SEM morphologies of zeolite T synthesis at different synthesis condition. | 14 |
| Figure 2.9 | The XRD diffractograms of each sample prepared by Rad et al., (2012), whereas T = zeolite T, L = zeolite L and W = zeolite W respectively. | 16 |
| Figure 2.10 | The XRD diffractograms of zeolite T prepared in different moles amount of water. (Source: Yin et al., 2015). | 19 |
| Figure 2.11 | Morphologies of zeolite T (a) without TMAOH (192 h) and (b) 0.05 TMAOH (48 h) (Source: Yin et al., 2015). | 20 |
| Figure 2.12 | The diffractograms of zeolite T samples prepared at different range of TMAOH synthesized at 373 K for 48 h (Source: Yin et al., 2015). | 21 |
| Figure 2.13 | Morphologies of zeolite T pumpkin-like shape crystals synthesized using double-template method | 22 |
Figure 2.14 The ternary composition systems of synthesized zeolite T, L and W from their respective researchers.

Figure 2.15 Ion exchange between nanoparticles of Au ion and zeolite L. (Source: Zeng et al., 2014).

Figure 2.16 SEM morphologies of zeolite L from recent literatures with respect of their formulations.

Figure 2.17 SEM morphologies of zeolite W from recent literatures with respect of their formulations.

Figure 2.18 Analysis of global temperature trends from 1950 to 2014 whereas the new analysis was conducted in 2015. Adapted from: "The recent global surface warming hiatus: Fact or artifact of data biases?" Science, 2015. (Source: NOAA's National Centers for Environmental Information, 2015).

Figure 2.19 World GHG (greenhouse gas) emission flow chart from the greenhouse gases emitted during 2010 (Source: ECOFYS, 2012).

Figure 2.20 The breakthrough curves of CO₂ and CH₄ using zeolite T as adsorbents (Source: Rad et al., 2012).

Figure 2.21 The schematic diagram of apparatus used for dynamic adsorption of binary gas (Source: Jiang et al., 2013).

Figure 2.22 The layers of tetrahedral and octahedral sheet arranged alternately (Source: Murray, 2000a).

Figure 2.23 The morphology of kaolinite (Source: Murray, 2000a).

Figure 2.24 The transformation of kaolinite into different silica groups during dehydroxylation (Source: Murray, 2006).

Figure 2.25 Schematic diagram of kaolinite alumino-silica layers of 1:1 and the position of H-atoms (inner H-atoms and inner surface H-atoms). (Source: White et al., 2013).

Figure 2.26 The illustration of diffraction pathway and the diffraction measure is measure from horizontal planes only. (Adapted from Creative Commons All
Figure 2.27 The schematic diagram of X-ray Powder Diffraction Analyzer and the rotation of detector during measuring angle of 2θ. (Adapted from Creative Commons Attribution-Noncommercial-Share Alike 2.5 License).

Figure 2.28 Diffraction patterns of different phase of SiO₂ namely cristobalite, quartz and glass respectively. (Adapted from Speakman, Massachusetts Institute of Technology).

Figure 2.29 Schematic diagram of SEM. (Source: Hafner, 2007).

Figure 2.30 The schematic diagram of gas adsorption from (a) Langmuir theory of monolayer adsorption and (b) multilayer adsorption by BET theory (Source: Hwang, 2011).

Figure 2.31 The schematic diagram of quadrupole concept of mass spectrometer in TPD. (Source: Chottiner & Giltinan, 2013).

Figure 2.32 The schematic diagram of three different desorption that can be obtained using TPD analysis (Source: University of Delaware, n.d).

Figure 3.1 Schematic methodology flow for synthesis zeolite T.

Figure 4.1 TGA curve for dehydroxylation of kaolin with temperature from 30 – 750 °C.

Figure 4.2 XRD diffractograms of kaolin and metakaolin treated at 750 °C for 4 hours.

Figure 4.3 The three main stages of crystallization process according to supersaturation level (Noble et al., 1997).

Figure 4.4 XRD diffractograms of samples prepared at 90 °C for time of 96 h, 120 h, 144 h, 168 h and 192 h respectively.

Figure 4.5 The morphologies of samples synthesized at temperature of 90 °C at different time of (c) 144 h, (d) 168 h, and (e) 192 h respectively.

Figure 4.6 XRD diffractograms of samples prepared at 100 °C.
for time of 96 h, 120 h, 144 h, 168 h and 192 h respectively.

Figure 4.7 The morphologies of samples synthesized at temperature of 100 °C at different time of (a) 96 h, (b) 120 h, (c) 144 h, (d) 168 h respectively.

Figure 4.8 XRD diffractograms of samples prepared at 110 °C for time of 96 h, 120 h, 144 h, 168 h and 192 h respectively.

Figure 4.9 The morphologies of samples synthesized at temperature of 110 °C at different time of (a) 96 h, (b) 120 h, (c) 144 h, (d) 168 h, and (e) 192 h respectively.

Figure 4.10 XRD diffractograms of samples prepared at time of 144 h 100 °C for crystallization temperature of 90 °C, 100 °C, and 110 °C respectively.

Figure 4.11 XRD diffractograms of samples prepared at time of 96 h for crystallization temperature of 90 °C, 100 °C, and 110 °C respectively.

Figure 4.12 XRD diffractograms of samples prepared at time of 168 h for crystallization temperature of 90 °C, 100 °C, and 110 °C respectively.

Figure 4.13 XRD diffractograms of free-template samples and samples prepared with TMAOH ranged from 0.05, 0.10, 0.15, 0.20 and 0.25 respectively.

Figure 4.14 The mechanisms of TMA+ cation in rearrange the silica into secondary unit and nucleation phase (Trinh et al., 2015).

Figure 4.15 The morphologies of samples synthesized with TMOAH at range of (a) 0.05, (b) 0.10, (c) 0.15, (d) 0.20.

Figure 4.16 FESEM images of nanoparticles of zeolite T prepared with 0.25 TMAOH

Figure 4.17 XRD diffractograms of free-template samples and samples prepared with TEAOH ranged from 0.05, 0.10, 0.15, 0.20 and 0.25 respectively.

Figure 4.18 The morphologies of samples synthesized with TEOAH at range of (a) 0.05, (b) 0.10, (c) 0.15, (d)
0.20, and (e) 0.25 respectively.

Figure 4.19 The molecular structure of TEA$^+$ ion.

Figure 4.20 Molecular structure for TBA$^+$ ion.

Figure 4.21 XRD diffractograms of free-template samples and samples prepared with TBAOH ranged from 0.05, 0.10, 0.15, 0.20 and 0.25 respectively.

Figure 4.22 SEM images for all samples prepared with TBAOH ratio at (a) 0.05, (b) 0.10, (c) 0.15, (d) 0.20, (e) 0.25 respectively.

Figure 4.23 SEM images of acicular or needle-like of samples prepared with (f) 0.15 TBAOH, (g) 0.20 TBAOH.

Figure 4.24 $N_2$ adsorption/desorption of zeolite T prepared from kaolin (c) without SDA, free template and, (a) with SDA, 0.05.

Figure 4.25 $N_2$ adsorption/desorption of zeolite T prepared from kaolin with SDA, (d) 0.10 and (e) 0.25 TEAOH.

Figure 4.26 $N_2$ adsorption/desorption of zeolite T prepared from kaolin (f) with SDA, 0.10 TBAOH.

Figure 4.27 Illustration of adsorption and desorption kinetics of carbon dioxide gas on the surface of zeolite T.

Figure 4.28 Desorption curves of zeolite T with different ratio of TMAOH.

Figure 4.29 Desorption curves of zeolite T with different ratio of TEAOH and TBAOH.
# List of Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>Alpha</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>β</td>
<td>Beta</td>
</tr>
<tr>
<td>°C</td>
<td>Degree Celcius</td>
</tr>
<tr>
<td>%</td>
<td>Percentage</td>
</tr>
<tr>
<td>μm</td>
<td>Micrometer</td>
</tr>
<tr>
<td>μmol/g</td>
<td>Volume of gas</td>
</tr>
<tr>
<td>2θ</td>
<td>2 theta</td>
</tr>
<tr>
<td>8MR</td>
<td>Eight membered rings</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Aluminum oxide</td>
</tr>
<tr>
<td>AlO₄</td>
<td>Aluminate</td>
</tr>
<tr>
<td>Au</td>
<td>Aurum (gold)</td>
</tr>
<tr>
<td>b.p</td>
<td>B.P. (Boling point)</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>CDM</td>
<td>Ceramic density mismatch</td>
</tr>
<tr>
<td>CH</td>
<td>Conventional hydrothermal heating</td>
</tr>
<tr>
<td>CH₄</td>
<td>Methane gas</td>
</tr>
<tr>
<td>cm³/G</td>
<td>Density</td>
</tr>
<tr>
<td>Co.</td>
<td>Company</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide gas</td>
</tr>
<tr>
<td>CR</td>
<td>Conventional refluxing heating</td>
</tr>
<tr>
<td>D₆R</td>
<td>Double 6 rings</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene glycol</td>
</tr>
<tr>
<td>ERI</td>
<td>Erionite</td>
</tr>
<tr>
<td>et al</td>
<td>And friends</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscope</td>
</tr>
<tr>
<td>H</td>
<td>Hour</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>H₂O/Al₂O₃</td>
<td>Water to alumina ratio</td>
</tr>
<tr>
<td>I₀</td>
<td>Intensity</td>
</tr>
<tr>
<td>IPCC</td>
<td>Inter-government panel on climate change</td>
</tr>
<tr>
<td>K</td>
<td>Potassium</td>
</tr>
<tr>
<td>K⁺</td>
<td>Potassium ion</td>
</tr>
<tr>
<td>K₂O</td>
<td>Potassium oxide</td>
</tr>
<tr>
<td>keV</td>
<td>Kilo electron volt</td>
</tr>
<tr>
<td>MER</td>
<td>Merlionite</td>
</tr>
<tr>
<td>MH</td>
<td>Microwave hydrothermal heating</td>
</tr>
<tr>
<td>min</td>
<td>Minute</td>
</tr>
<tr>
<td>MR</td>
<td>Microwave refluxing heating</td>
</tr>
<tr>
<td>N₂</td>
<td>Nitrogen gas</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Sodium ion</td>
</tr>
<tr>
<td>Na₂O</td>
<td>Sodium oxide</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>NOAA's</td>
<td>National oceanic and atmospheric administration</td>
</tr>
<tr>
<td>OFF</td>
<td>Offretite</td>
</tr>
</tbody>
</table>

XVII
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pa</td>
<td>Pascal</td>
</tr>
<tr>
<td>PV</td>
<td>Pervaporation</td>
</tr>
<tr>
<td>PVA</td>
<td>Polyvinyl alcohol</td>
</tr>
<tr>
<td>SDA</td>
<td>Structure directing agents</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>Si/Al</td>
<td>Silica/alumina</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Silicon oxide</td>
</tr>
<tr>
<td>SiO₄</td>
<td>Silicate</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>t (h)</td>
<td>Time (hour)</td>
</tr>
<tr>
<td>TBA⁺</td>
<td>Tetrabutylammonium ion</td>
</tr>
<tr>
<td>TBAOH</td>
<td>Tetrabutylammonium hydroxide</td>
</tr>
<tr>
<td>TEA⁺</td>
<td>Tetraethylammonium ion</td>
</tr>
<tr>
<td>TEAOH</td>
<td>Tetraethylammonium hydroxide</td>
</tr>
<tr>
<td>TPA⁺</td>
<td>Tetrapropylammonium ion</td>
</tr>
<tr>
<td>TMA⁺</td>
<td>Tetramethylammonium ion</td>
</tr>
<tr>
<td>TMAOH</td>
<td>Tetramethylammonium hydroxide</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature-programmed desorption</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultrahigh vacuum</td>
</tr>
<tr>
<td>VP</td>
<td>Vapor permeation</td>
</tr>
<tr>
<td>wt%</td>
<td>Weight percentage</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
</tbody>
</table>
# LIST OF APPENDICES

<table>
<thead>
<tr>
<th>APPENDIX</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Determination of formulation for zeolite T using Metakaolin.</td>
<td>136</td>
</tr>
<tr>
<td>B</td>
<td>Determination of SDA's volume with respect of the zeolite T formula.</td>
<td>137</td>
</tr>
<tr>
<td>C</td>
<td>Preparation of zeolitization of zeolite T from metakaolin via conventional hydrothermal.</td>
<td>140</td>
</tr>
</tbody>
</table>
1.1 Study Background

First natural zeolite discovered by Swedish mineralogist Cronstedt but there is no documented proven and in 1792, the first clearly identified zeolite discovered was chabazite (Biercuk & Reilly, 2010). Zeolite material have long been considered as attribution in purification and separation of gas (Ackley et al., 2003) and historically consist of two types, which are natural zeolites and engineered zeolites. Natural zeolites occurred abundantly in nature including phillipsite, ferrierite, mordenite, clinoptilolite, chabazite and erionite (Ackley et al., 2003) and this type of zeolites are practically well suited in removing trace-gas (Ackley et al., 2003).

However, large scale of natural zeolites from deposited minerals are difficult to obtain and it can have varied chemical composition even mined at same location. The outcome from the usage of zeolite must be fulfilled whether it's natural or synthetically engineered, are useful candidates in purification and separation of gas or other adsorptive applications.

Meanwhile, over 176 different framework types of zeolite engineered by manipulating the chemical composition combined by alumino-silicate tetrahedral layers (Qin et al., 2014). The zeolite framework has an overall negative charge resulting from the net charge of alumina tetrahedral layer of -1, while the silica tetrahedral in the framework have zero charge.

Therefore, in order to balance the charge, extra-framework cations (usually monovalent ions) such as Na$^+$ and K$^+$ are present as part of the zeolite. These monovalent ions sit in specific sites within the pores in the structure to ensure the framework charge is balanced. Shared by oxygen atom as bridges of the layers –
zeolites has diverse channels which contributes to it varied of applications. Generally, the unique environment exhibits by the synthetic zeolites are contributed from zeolite framework and its pore size because within zeolites, electrons may be transferred and zeolites may act as electron donor or acceptor (Liu et al., 2015). One of the example of engineered zeolite derived from natural occurring material is zeolite T. The zeolite T was firstly introduced by Bennet and Grad (Gorring, 1973) and it is belongs to the intergrowth of two closely related natural mineral of the offretite and erionite, due to the similarities in their stacking faults of natural and synthetic forms.

In 2015, National Oceanic and Atmospheric, NOAA’s National Centers for Environmental Information has conducted new analysis regarding the rate of global warming. Rate of global warming increased from year 1950 – 1999, and in year 2000 – 2014, the temperature trends dropped indicating the hiatus pattern of global warming. However, recent analysis in year 2015 has proclaimed that the slowdown or hiatus pattern of global temperature from year 2000 – 2014 which shows that the rate of global warming has continued and increasing.

Meanwhile, 97% of climate based research papers claiming the position of human-caused global warming whereas the human and their activities are the cause of the increasing of greenhouse gases (The Consensus Project, 2015). The greenhouse gases of carbon dioxide gas (CO₂) are majorly contributed by the industrial activities (ECOFYS, 2010). Therefore, the development of cost-effective CO₂ capture technologies has attracted intensives attention in decades (Jiang et al., 2013).

For the past decades, medium that were used to capture CO₂ was organic polymer based material due to the economically cost. However, the organic polymer has low selectivity at high temperature where it is severed by decomposition. The organic polymer suffer swelling-induced plasticization by CO₂ and hydrocarbon incorporation (Yin et al., 2013; Mayur et al., 2011; Brunetti et al., 2010; Wind et al., 2004; Powell & Qiao, 2006; Sebastian et al., 2006).
Therefore, the organic polymer has currently being replace by inorganic zeolite material. Subsequently, study conducted by Jiang et al., (2013) has proved the potential of the zeolite T as an efficient absorbent in trapping CO₂/CH₄ and CO₂/N₂ for natural gas purification. Due to its stability against high acidity surroundings (Cui et al., 2004) and ability to maintain hydrophilic properties at high thermal surroundings (Mirfendereski et al., 2008; Rad et al., 2012; Zhou et al., 2008; Zhou et al., 2009; Yin et al., 2013; Jiang et al., 2013), zeolite T has offer potential application in membrane separators for gas, vapor and liquid phase (Lin et al., 2002).

Despite the overwhelming researches and study regarding zeolite T and the potential applications, there was been no study conducted on the pathway providing in synthesizing zeolite T from clay especially kaolin. Kaolin is a material that contain stable layer of silica and alumina.

The utilization of kaolin are possible by converting the stable form into an active amorphous of metakaolin which are proven as suitable natural resource for synthesizing various types of zeolites (Johnson & Arshad, 2014). Hence, this study provides the synthesis pathways in developing molecular absorbent of zeolite T from metakaolin with and without structure directing agents as a template.

1.2 Research Objectives

The objectives of this study are:

a) To synthesis and characterize the free-template zeolite T from metakaolin in conventionally hydrothermal method.

b) To synthesis and determine the crystallization of zeolite T from metakaolin in presence of three different structure directing agents of tetramethylammonium hydroxide (TMAOH), tetraethylammonium hydroxide (TEAOH) and tetrabutylammonium hydroxide (TBAOH).

c) To determine the efficiency of zeolite T as absorbent for CO₂ gas adsorption-desorption.
1.3 Problem Statement

Development in synthesized zeolite T has extended toward various industrial applications especially in gaseous adsorption. However, the recent synthesis parameters necessitate high cost in the utilization of pure reagent of silica and alumina as the starting material. An economical measure to synthesis pure zeolite T from natural resource is a must in order to improve the current procedures. Moreover, the lack of in-depth information regarding crystal evolution phase of co-exist type zeolite T L and W in past research work are incontestable. The potential application toward adsorption of CO2 by newly synthesized zeolite T from economical source should be determine in order to provide well-structured date for comparison of newly synthesized metakaolin based zeolite T with the current zeolite T.

1.4 Scope of Research

Chapter 1 briefly elucidates the history of zeolite T and the application towards overcoming the greenhouse gas. It also accentuate the reason of this project in synthesis zeolite T from kaolin. Past researches and findings are featured in Chapter 2 whereas the priority are given to the recent parameters conditions and potential applications of zeolite T. Chapter 3 present methodology that were conducted whereas parameters such as synthesis temperature, time, SDA used in synthesis of the zeolite T and the characterization of the zeolites. Chapter 4 elucidate the results and discussion of crystal behavior of zeolite synthesized. It will include the outcomes of the synthesis conditions and characterization of kaolin, metakaolin, samples of zeolite and potential application of zeolite T. The conclusion of the research study are summarized in Chapter 5.
REFERENCES


Chen, L. and Yan, B. 2014. Novel cool white-luminescent hybrids through host-guest assembly of 6-hydroxybenz[de]anthracen-7-one and europium ion exchange. *Inorganic Chemistry Communications*, **43**: 75-77.


122


Holmes, A. Synthetic and atomic force microscopy studies of Offretite/Erionite family zeolites, School of Chemistry, University of Manchester, United Kingdom, 2011.


Speakman, S. A. Basics of X-Ray powder diffraction- Training to become an independent user of the X-ray SEF at the Centre for Materials Science and Engineering at MIT. Massachusetts Institute of Technology.


Stach, H., Thamm, H., Fiedler, K., and Grauert, B. 1986. 7th International Zeolite Conference, Tokyo, 539.


