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

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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.

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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 (CO_2) 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 SiO_2:Al_2O_3:Na_2O:K_2O:H_2O (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-desorbtion of zeolite T (correspond to different SDA) toward CO_2 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 m^2/g and 24.96 Å respectively, shows an excellent adsorption-desorption by able to adsorbed 4893 μmol/g of CO_2 and fully desorbed at temperature 907 °C.

ABSTRAK

SINTESIS HIDRTOTERMA ZEOLITE T BERASASKAN METAKAOLIN DENGAN TIGA JENIS EJEN PENGSTRUKTURAN KHUSUS DAN KAPASITI PENJERAPAN TERHADAP GAS KARBON DIOKSIDA

Teknologi dalam menjerap gas karbon dioksida melalui bahan zeolit sintetik telah menjadi satu penemuan selama beberapa dekad yang lalu. Walau bagaimanapun, terdapat halangan dalam penyedian bahan baru untuk sintesis zeolit dan biasanya melibatkan kos reagen yang tinggi. Oleh itu, penyelidikan ini memberi tumpuan untuk mengatasi batasan kajian dan mengembangkan teknologi baru di dalam bidang sintesis dan kegunaan zeolit T dari metakaolin untuk penjerapan karbon dioksida (CO_2). Metakolin (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 hidrotemma dengan nisbah molar SiO_2: Al_2O_3: Na_2O: K_2O: H_2O (1: 0.04: 0.26: 0.09: 14), manakala beberapa parameter tindak balas seperti suhu, masa tindakbalas, jenis ejen pengstrukturan khusus, SDA (TMOAH, TEAOH, dan TBAOH) telah dikaji. Tambahan pula, sifat-sifat poros dan penjerapan-penyahjerapan zeolit T (berdasarkan SDA yang berbeza) terhadap CO_2 telah dijalankan. Keputusan XRD untuk Zeolit T yang disediakan dengan TMAOH mengikut nisbah yang berbeza (0.05 - 0.25) menunjukkan penghasialan hablur tulen zeolit T seperti beras dan saiz kristal adalah nano 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 spesies zeolit T yang wujud bersama-sama dengan zeolit L di dalam satu sistem. Manakala spesies zeolit W diperoleh pada nisbah maksima TEAOH (0.25). Sistem dengan TBAOH sebagai SDA telah menyebabkan pembentukan hablur jejarum yang tidak ketahui, serta penghabluran zeolit T yang negatif dan pembentukan hablur zeolit L yang tidak stabil pada nisbah 0.10. Ia juga memmbentuk penghabluran yang lemah pada nisbah 0.05, 0.15, 0.20, dan 0.25. Zeolit T yang tulen dengan nisbah terendah 0.05 TMAOH mempunyai luas permukaan 357.9 m^2/g dan saiz liang 24.96 Å, ia menunjukkan penjerapan-penyahjerapan yang unggul dengan menjerap CO_2 sebanyak 4893 μmol/g dan penyahjerapan sepenuhnya pada suhu 907 °C.

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α	Alpha
Ǻ	Angstrom
β	Beta
$^{\circ}C$	Degree celcius
%	Percentage
μm	Micrometer
$\mu mol/g$	Volume of for gas
2θ	2 theta
8MR	Eight membered rings
Al_2O_3	Aluminum oxide
AlO_4	Aluminate
Au	Aurum (gold)
b.p	Boling point
BET	Brunauer-Emmett-Teller
CDM	Charger density mismatch
CH	Conventional hydrothermal heating
CH4	Methane gas
cm^3/G	Density
Co.	Company
CO2	Carbon dioxide gas
CR	Conventional refluxing heating
D6R	Double 6 rings
EG	Ethylene glycol
ERI	Erionite
et al	And friends
FESEM	Field emission scanning electron microscope
H	Hour
H_2O	Water
H_2O/Al_2O_3	Water to alumina ratio
I_o	Relative intensity
IPCC	Inter-government panel on climate change
K	Potassium
K^+	Potassium ion
K_2O	Potassium oxide
keV	Kilo electron volt
MER	Merlionite
MH	Microwave hydrothermal heating
min	Minute
MR	Microwave refluxing heating
N_2	Nitrogen gas
Na^+	Sodium ion
Na_2O	Sodium oxide
nm	Nanometer
NOAA's	National oceanic and atmospheric administration
OFF	Offretite

Pa	Pascal
PV	Pervapoaration
PVA	Polyvinyl alcohol
SDA	Structure directing agents
SEM	Scanning electron microscopy
Si/Al	Silica/alumina
SiO_2	Silicon oxide
SiO_4	Silicate
T	Temperature
t (h)	Time (hour)
TBA^+	Tetrabutylammonium ion
TBAOH	Tetrabutylammonium hydroxide
TEA^+	Tetraethylammonium ion
TEAOH	Tetraethylammonium hydroxide
TPA^+	Tetrapropylammonium ion
TMA^+	Tetramethylamonium ion
TMAOH	Tetramethylammonium hydroxide
TPD	Temperature-programmed desorption
UHV	Ultrahigh vacuum
VP	Vapor permeation
wt%	Weight percentage
XRD	X-ray Diffraction

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CHAPTER 1

INTRODUCTION

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 (CO_2) are majorly contributed by the industrial activities (ECOFYS, 2010). Therefore, the development of cost-effective CO_2 capture technologies has attracted intensives attention in decades (Jiang *et al.,* 2013).

For the past decades, medium that were used to capture CO_2 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 CO_2 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 CO_2/CH_4 and CO_2/N_2 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 CO_2 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.

CHAPTER 2

LITERATURE REVIEW

2.1 Zeolite T: First generation zeolites

Zeolite T is classified as one of the important member of first generation of zeolite, intergrowth type of zeolite T was genuinely introduced by Bennet and Gard (Gorring, 1973; Rad *et al.,* 2012). Three dimensional framework of tetrahedral layer of SiO_4 linked with AlO_4 stacked with chabazite group of offretite (OFF) and erionite (ERI) in a random layer arrangement. The position of offretite and erionite enable zeolite T to possess unique properties which has contributed into different field of applications.

Zeolite T with intermediate 3:4 of Si/Al are reported with presence of hexagonal crystal structure of OFF and ERI in arrangement of AABAACAABAAC.. instead of AABAABAAB.. of original three dimensional framework of tetrahedral SiO_4 and AlO_4 (Mougenel & Kessler, 1991). Stacking arrangement of additional crystal structure to the former framework disable the formation of large void or channel within the structure of ERI which indirectly gives zeolite T the properties of voids size variations.

Structure of hexagonal crystal of OFF and ERI are shown in Figure 2.1 represent linked system of zeolite T with oxygen atoms are neglected while Si and Al atoms are bonded at the corners of the polyhedral. Meanwhile, the framework structure for both OFF and ERI are shown in Figure 2.2 and 2.3 respectively.