HYDROTHERMAL SYNTHESIS AND CHARACTERIZATION OF ZSM-5 ZEOLITE USING KAOLIN

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ABSTRACT

Zeolites have made an impact in the field of materials and catalysis in the past 50 years. ZSM-5 zeolite has been widely used in petrochemical industry due to its unique 10 membered ring pore opening that has the shape selectivity properties. Raw clay such as kaolin is an excellent aluminosilicate source for the synthesis of zeolite because the clay is rich in aluminium oxide and silicon dioxide. The ZSM-5 zeolite was synthesized by using hydrothermal method. In this study, the parameters of the synthesis were crystallization time and temperature ranging from 12 hours to 36 hours and 120°C to 180°C respectively. Due to the absence of XRD, only SEM and FTIR were used to characterize the samples. Images of SEM did not significantly show any formation of ZSM-5 zeolite. However, the IR spectra show the formation of band at 542cm^{-1} in the sample synthesized with crystallization time of 36 hours and temperature of 180°C. This shows that the long crystallization time and high temperature favour the formation of ZSM-5 crystalline structure.

SINTESIS HIDROTERMA DAN PENCIRIAN ZSM-5 ZEOLITE DARIPADA KAOLIN

ABSTRAK

Zeolite telah memberi impak dalam bidang bahan dan pemangkinan dalam tempoh 50 tahun yang lalu. Oleh sebab keunikan ZSM-5 zeolite yang memiliki pembukaan liang yang dibina oleh 10 anggota, ZSM-5 zeolite mempunyai sifat pemilihan dan digunakan secara luas dalam industri petrokimia. Tanah liat mentah seperti kaolin adalah sumber aluminosilikat yang baik untik sistesis zeolite kerana tanah liat kaya dengan aluminium oksida dan silicon dioksida. ZSM-5 zeolite telah disistesis dengan menggunakan kaedah hidroterma. Dalam kajian ini, parameter untuk sintesis adalah masa dan suhu penghabluran di antara 12 jam hingga 36 jam dan 120°C hingga 180°C masing-masing. Oleh kerana ketiadaan XRD, hanya SEM dan FTIR digunakan untuk proses pencirian. Imej SEM tidak menunjukan sebarang pembentukan ZSM-5 zeolite dengan ketara. Walau bagaimanapun, spektrum IR menunjukkan pembentukan band di 542cm^{-1} dalam sampel yang telah disintesiskan dengan masa penghabluran 36 jam dan suhu 180°C. Ini menunjukkan bahawa masa penghabluran yang panjang dan suhu yang tinggi adalah lebih sesuai untuk pembentukan struktur kristal ZSM-5.

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LIST OF SYMBOLS AND ABBREVIATIONS

FTC	Framework-type code
FTIR	Fourier transform infrared spectroscopy
ICDS	Inorganic Crystal Structure Database
LTA	Linde Type A
PET	Polyethylene terephthalate
PXRD	Powder X-ray Diffractometer
SEM	Scanning electron microscope
TGA	Thermogravimetry Analysis
TPAOH	Tetrapropylammonium hydroxide
XRD	X-ray diffraction
ZSM-5	Zeolite Socony Mobil-5
θ	Theta
λ	Wavelength

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Zeolite mineral was first found by a Swedish mineralogist, Cronstedt in 1756. The zeolite mineral found was known as stilbite. The name "zeolite" came from two Greek words, *zeo* and *lithos* which means "to boil" and "stone" respectively (Cronstedt, 1756). The first synthetic zeolites were discovered by Milton, Breck and co-worker at Union Carbide. Modern Latin alphabet such as A, B, X, Y, and L is used to name the zeolites (Johnson & Arshad, 2014).

Zeolites have made an impact in the field of materials and catalysis in the past 50 years. The very first description of zeolites can be traced back to about 250 years ago, but the last 50 years experienced high zeolite research activities. As the result, almost 200 different structural types of zeolites have been successfully synthesized (Čejka *et al.*, 2010). There is a total of 225 framework type codes has been approved by the Structure Commission (International Zeolite Association, 2014). Every framework which has different topologies with distinct pore size and architecture can vary in chemical composition (Bulut *et al.*, 2009).

Zeolites are known as tetrahedrally connected framework solids with silica base. The structural formula of a zeolite is based on the crystallographic unit cell, represented by:

$$(M^{n+})_{x/n}[(AlO_2)_x(SiO_2)_y]\cdot wH_2O \qquad (1.1)$$

Where M represents the exchangeable cation of valence n, M is generally a Group I or II cation. y/x represents the Si/Al ratio of the zeolite, and w represents the water contained inside the discrete size cages or channels of zeolites. The framework of zeolites is composed of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra, cages that connected by pores are formed by the linking tetrahedra (Ríos *et al.*, 2009). Zeolites have structures consist of channels and cages large enough to contain extra-framework cations and able to adsorb and desorb molecules with the size range of hydrogen to complex organics up to 1nm (Wright & Pearce, 2010). Due to the high cation exchange capacity, their large surface area, and their structural characteristics which facilitate pollutant absorption and encapsulation, zeolites are very useful in environmental applications (Belviso *et al.*, 2013). Despite the many useful properties of zeolites, only a limited number of zeolite topologies are currently used in the major industrial processes. The zeolites that have industrial application including zeolite X, Y (FAU), ZSM-5 (MFI), mordenite (MOR), zeolite Omega (MAZ), and zeolite Beta (BEA) (Bulut *et al.*, 2009).

The microporosity of zeolites gives them adsorption, catalytic, and ion-exchange properties. However, nowadays study on new zeolite application such as green chemistry, hybrid materials, medicine, and nanotechnology is given much more attention. In medical applications, zeolites are considered as drug delivery systems due to the capacity of their adsorption selectivity and being able to control the release of various kinds of ions. This property of zeolites can be enhanced or modified by adding surfactants on the external surface (Rivera *et al.*, 2003). For example, zeolite X crystals (Rimoli *et al.*, 2008) or ZSM-5 microspehere (Wong, 2006) which are stable at low pH condition release ketoprofen and biotin respectively in gastrointestinal applications. Furthermore, CAN-type zeolite can store and release tetractcycline antacid to control the pH in the stomach (Linares & Brikgi, 2006; Linares *et al.*, 2004). Other application such as the delivery of antitumoral drug was proposed using zeolite CuX. Zeolites also show potential in the loading and release of doxorubicin as a type of magnetic drug delivery (Sebastián *et al.*, 2010).

In this study, ZSM-5 zeolite will be synthesized. ZSM-5 zeolite was first prepared by Argauer and Landolt in 1971 (Argauer & Landolt, 1972). ZSM-5 has been widely used as sorbents and catalyst due to its unique channel structure, thermal stability, acidity, and shape selectivity property (Khatamian & Irani, 2009). ZSM-5 has the structure type of MFI which its pathway of the crystallization process, morphology, and singular properties are influenced by variables such as, the ratio of silicon and aluminum source, the ratio of template and silicon, and the alkalinity (Lowe, 1988; Nastro *et al.*, 1984; Petrik *et al.*, 1995). The particle size of the zeolite is affected by the ratio of the sources as well (Tosheva & Valtchev, 2005). ZSM-5 zeolite is well known of its application in petrochemical processing, fine chemical production, and liquid-gas separation (Kumar *et al.*, 2002).

The alumina source used in this study is kaolin. Clay minerals used as the raw materials in the synthesis of zeolites has been first recorded in 1961 (R. M. Barrer & Denny, 1961). By using cheap raw material such as kaolin to synthesize zeolite have the economic advantages compared to using standard synthetic chemicals which are very costly (Kovo *et al.*, 2009). Kaolin is one of the earth most abundant minerals and it has the silica and alumina ratio which is very similar to zeolites. By undergoing hydrothermal treatment, kaolin can be converted to zeolites (Alkan *et al.*, 2005).

A significant progress can be seen in the past few years in the synthesis of zeolite materials and their applications. However, problems regarding reproducibility have not been solved (Sebastián *et al.*, 2010). The supporting material in the synthesis of zeolites plays an important role in producing either very disordered material such as a typical catalyst-support like amourphous silica or a highly ordered material like a mesoporous molecular sieve. Nature of the support material or known as template is depended in producing intercrystalline or intracrystalline zeolites. Templating are forming hierarchical zeolite materials by fusing a template mesoporous material into zeolite to enable an ordered transformation of hierarchical zeolite or through a controlled deposition of zeolite on a templated material. There are few preparative methods available for synthesizing zeolites including solid templating, supramolecular templating, and indirect templating (Egeblad *et al.*, 2007). In this study, the indirect templating method will be used to synthesize zeolites.

1.2 Objectives of the Study

The objectives of this study are:

i. to synthesize ZSM-5 zeolite from kaolin using TMAH as template,
ii. to characterize the synthesized ZSM-5 zeolite by using XRD, SEM, FTIR, and
iii. to study the effect of temperature and crystallization time on the synthesis of ZSM-5 zeolite

1.3 Scope of the Study

In this study, ZSM-5 zeolite will be synthesized using hydrothermal treatment as suggested by Khatamian & Irani (2009). Raw kaolin will be calcined at 700°C based on the method suggested following by the addition of silica source from silicon dioxide to the mixture (Feng *et al.*, 2009b). The mixture is then mixed with tetramethylammonium hydroxide (TMAH) as template and distilled water. Sodium hydroxide (NaOH) is added to the mixture and mixed. The mixture is heated in a Teflon bottle at the temperature ranging from 120°C to 180°C for crystallization process. A sample is removed from the bottle to be analyzed by FTIR on certain period of time between 12 hours to 36 hours of crystallization time. The crystallinity and surface morphology of the zeolite will be determined using XRD and SEM respectively.

CHAPTER 2

LITERATURE REVIEW

2.1 Zeolites

Zeolite mineral is basically composed of AlO_4 and SiO_4 tetrahedra. These tetrahedra linked to one another by sharing the oxygen atoms to form interconnected cages and channels with pore sizes ranging between 4 – 12 Å (Ward, 1967). This is how the three-dimensional framework structure of the zeolite is formed. These structures usually contain mobile water molecules, alkali metal cations from group 1A such as sodium, potassium, lithium, and cesium cations. They can also contain alkaline earth metal cations from group 2A such as calcium, strontium, barium, and magnesium cations. However, aluminum and silicon in the zeolite can be replaced by elements such as phosphorus and beryllium (Tschernich, 1992). In most zeolite structures, the AlO_4 and SiO_4 tetrahedra which are the primary structural units will assemble and form secondary building units. These units may be cubes, hexagonal prims, or cubo-octahedra (Jacobs *et al.*, 2001).

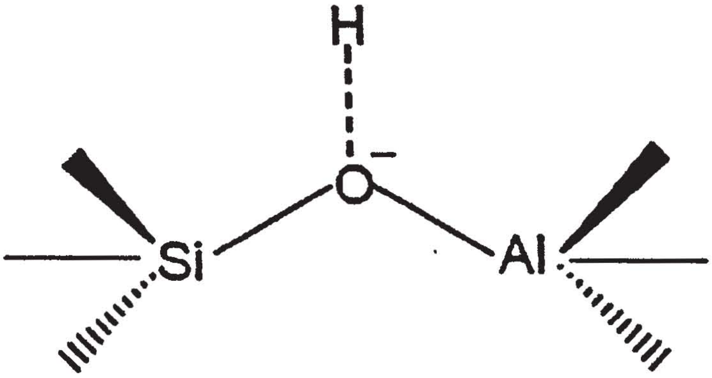

Figure 2.1. Basic chemical structure of zeolites (Haag *et al.*, 1984).

2.1.1 History of Zeolites

The first zeolite discovery was in 1756 by a Swedish mineralogist (Cronstedt, 1756). Zeolites are categorized as one of the crystalline aluminosilicate minerals and the deposition of zeolite minerals was found mostly close by the volcanic area. There are around fifty species of natural zeolites that are known with various chemical composition and structure. However, the major part of volcano-sedimentary deposits are consisted of only eight zeolite minerals. The eight natural zeolites are analcime, chabazite, clinoptilolite-heulandite, erionite, ferrietite, laumontite, mordenite, and philipsite (Win, 2004).

In 1840, the ability of zeolite crystals to reversibly dehydrate without apparent change in transparency or morphology is observed by Damour. In 1896, after observing various liquids such as alcohol, benzene, and chloroform were occluded by dehydrated zeolite crystals, Friedel suggested that the structure of dehydrated zeolites consists of open spongy framework. The first structure of zeolites were determined by Taylor and Pauling in 1930. By the mid 1930's to 1940's, the work of synthesis and characterization of zeolites has been well known.

The study in zeolite synthesis in searching of new approaches for air separation and purification was initiated by the Linde Division of Union Carbide Corporation. The commercial zeolites type A, X, and Y were discovered by R. M. Milton and D.W. Breck in between 1949 to 1954. Following by Mobil Oil introduced the use of zeolite X in catalytic cracking in 1962 and the synthesis of the high silica zeolites such as zeolite beta and ZSM-5 was reported from 1967 to 1969.

In the past century, the discovery of new compositions and structures of molecular sieves encouraged the synthesis of new zeolites. Zeolites of various structure types have been discovered since 1978, however, the as-synthesized guest species are not stable to remove, especially water and organic templates, hence, the synthesized zeolites cannot adsorb molecules reversibly and the catalytic reaction cannot be carried out. There were some extensive work carried out on the synthesis and applications of ZSM-5 and other members of the high silica zeolite family (Jacobs *et al.*, 2001).

2.1.2 Types of Zeolites

In the evolution of synthetic molecular sieve materials, zeolites are separated into three categories. Which are "Low" Si/Al Zeolites, such as Zeolite A and X, "Intermediate" Si/Al Zeolites, such as Zeolite Y, L, and omega, "High" Si/Al Zeolites, such as ZSM-5. The Si/Al ratio of zeolites mentioned are 1 to 1.5, 2 to 5, and 10 to 100 respectively (Moscou, 1991).

The structural characterization of zeolite crystals is based on the identification of the particular zeolite framework type. The framework type is assigned based on the zeolite database entries in the Inorganic Crystal Structure Database (ICSD). Both natural and synthetic zeolites are included in the entries. The applications of zeolites are strongly contingent to the framework topologies of zeolites. Therefore, the classification scheme that became the standard to identify zeolites from other zeolitic materials that display tetrahedral framework structures is based on the structure of the zeolite crystals. All the zeolite entries are tested by using a three-step process to determine the framework-type code (FTC) of the zeolites.

The three-step process includes, data verification on the entries concerning eventual typographical errors, missing atoms in the reduced unit cell, or unspecified mineral information in order to clearly identify their structure. Based on the symmetry information of the asymmetric unit cell in the database, the underlying frameworks of the crystalline structures were generated. This is to remove the atoms in the cation and adsorbent portions of the chemical formula and leave only the bare framework that contains only the tetrahedral atoms and oxygen. Lastly, all the bond lengths of tetrahedral and tetrahedral-oxygen in the bare underlying framework is checked (Yang *et al.*, 2010).

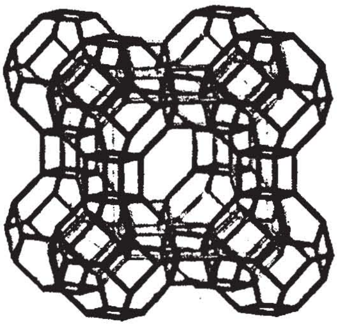

Figure 2.2. The framework structure of the zeolite LTA (Baerlocher *et al.*, 2007).

2.1.3 Applications of Zeolites

The many applications of zeolites are based on the various properties of the zeolite crystals. Natural zeolites are used as the particle reinforcement material in concrete or as a filler in paper making industry (Win, 2004). Synthetic zeolites are most commonly used as molecular sieves, catalysts, and ion-exchangers. Zeolites are more preferable than any other crystalline inorganic oxide-materials because of its unique combination of properties.

One of the properties is the microporous character with uniform pore dimensions. Due to this properties, zeolite crystals has the ability to allow certain hydrocarbon molecules to enter the crystals while rejects others molecules based on the molecular size. In this case, zeolite crystals are a very ideal and effective molecular sieve. Therefore, it is used in the adsorbents, desiccants, and separation processes. The application includes drying agents, gas purifier, and separator for n-paraffins and p-xylene from their isomers (Moscou, 1991).

The countercharge ions in the zeolite crystals have the ability to perform all types of ion-exchange reactions. These countercharge ions are normally Na^+, K^+, Ca^{2+} ions, but it can also be modified to H^+ or NH_4^+ ions (Ćurković *et al.*, 1997). Zeolites is used in water softening because of the cation of the zeolites will replace the heavy ions in the hard water. In water treatment process, sodium ions in the zeolites will replace the calcium and magnesium ions in the water. The ionic reaction is such as:

$$M^{2+} + 2\,Na^+ (Z^-) \rightleftharpoons 2\,Na^+ + M^{2+} (Z^-)_2 \tag{2.1}$$

Where M^{2+} represents calcium or magnesium ions, (Z^-) represents zeolites. The exchanged material can be regenerate by washing a concentrated sodium chloride solution (Win, 2004). As the result, zeolites are used in detergent, waste water and nuclear effluent treatment, and soil improvement. In the detergent formulation, zeolite A is used as a sequestering agent to substitute phosphates ions (Moscou, 1991). However, zeolites play an important role in agriculture by acting as a slow release mechanism of potassium and ammonium ions in the soil. The cation exchange

REFERENCES

Alkan, M., Hopa, Ç., Yilmaz, Z., & Güler, H. 2005. The effect of alkali concentration and solid/liquid ratio on the hydrothermal synthesis of zeolite NaA from natural kaolinite. *Microporous and Mesoporous Materials,* **86**(1–3), 176-184.

Argauer, R. J., & Landolt, G. R. (1972). Crystalline zeolite zsm-5 and method of preparing the same: Google Patents.

Baerlocher, C., McCusker, L. B., & Olson, D. H. (2007). *Atlas of zeolite framework types*: Elsevier.

Barrer, R. M. (1982). *Hydrothermal chemistry of zeolites*: Academic Press.

Barrer, R. M., & Denny, P. J. 1961. 202. Hydrothermal chemistry of the silicates. Part X. A partial study of the field CaO-Al_2O_3-SiO_2-H_2O. *Journal of the Chemical Society (Resumed)*(0), 983-1000.

Behrens, P. 1993. Modelling of structure and reactivity in zeolites. Edited by R. C. A. Catlow, Academic Press, London 1992, 260 pp., £ 45, ISBN 0-12-164240-6. *Advanced Materials,* **5**(6), 482-483.

Belviso, C., Cavalcante, F., Lettino, A., & Fiore, S. 2013. A and X-type zeolites synthesised from kaolinite at low temperature. *Applied Clay Science,* **80–81**(0), 162-168.

Breck, D. W. 1988. Zeolite molecular sieves, 1974. *New York,* 379-392.

Brigatti, M. F., Galán, E., & Theng, B. K. G. (2013). Chapter 2 - Structure and Mineralogy of Clay Minerals. In B. Faïza & L. Gerhard (Eds.), *Developments in Clay Science* (Vol. 5, pp. 21-81): Elsevier.

Broglie, L. d. 1924. XXXV. A tentative theory of light quanta. *Philosophical Magazine Series 6,* **47**(278), 446-458.

Brown, M. (1988). Thermogravimetry (TG) *Introduction to Thermal Analysis* (pp. 7-22): Springer Netherlands.

Bulut, Metin Jacobs, & A., P. (2009). Concepts for Preparation of Zeolite-Based Catalysts *Synthesis of Solid Catalysts* (pp. 241-276): Wiley-VCH Verlag GmbH & Co. KGaA.

Burton, A. W. (2009). Powder Diffraction in Zeolite Science. In A. Chester & E. G. Derouane (Eds.), *Zeolite Characterization and Catalysis* (pp. 1-64): Springer Netherlands.

Byrappa, K., & Yoshimura, M. (2013). 6 - Hydrothermal Synthesis and Growth of Zeolites. In K. Byrappa & M. Yoshimura (Eds.), *Handbook of Hydrothermal Technology (Second Edition)* (pp. 269-347). Oxford: William Andrew Publishing.

Cejka, J. (2005). *Zeolites and ordered mesoporous materials: progress and prospects: the 1st FEZA School on Zeolites, Prague, Czech Republic, August 20-21, 2005* (Vol. 157): Gulf Professional Publishing.

Čejka, J., Corma, A., & Zones, S. (2010). Front Matter *Zeolites and Catalysis* (pp. I-XX): Wiley-VCH Verlag GmbH & Co. KGaA.

Chandrasekhar, S., & Pramada, P. N. 2004. Kaolin-based zeolite Y, a precursor for cordierite ceramics. *Applied Clay Science,* **27**(3–4), 187-198.

Cheng, H., Liu, Q., Yang, J., Ma, S., & Frost, R. L. 2012. The thermal behavior of kaolinite intercalation complexes-A review. *Thermochimica Acta,* **545**, 1-13.

Chester, A. W., & Derouane, E. G. (2009). *Zeolite characterization and catalysis*. Springer.

Ciric, J. 1968. Kinetics of zeolite A crystallization. *Journal of Colloid and Interface Science,* **28**(2), 315-324.

Cronstedt, A. F. 1756. Ron och beskriting om en obekant barg ant, som kallas zeolites. *Akad. Handl. Stockh,* **18**(120-130).

Cubillas, P., & Anderson, M. W. (2010). Synthesis Mechanism: Crystal Growth and Nucleation *Zeolites and Catalysis* (pp. 1-55): Wiley-VCH Verlag GmbH & Co. KGaA.

Cundy, C. S., & Cox, P. A. 2003. The Hydrothermal Synthesis of Zeolites: History and Development from the Earliest Days to the Present Time. *Chemical Reviews,* **103**(3), 663-702.

Ćurković, L., Cerjan-Stefanović, Š., & Filipan, T. 1997. Metal ion exchange by natural and modified zeolites. *Water research,* **31**(6), 1379-1382.

Dai, F., Suzuki, M., & Saito, I. 1986. Mechanism of zeolite crystallization without using template reagents of organic bases. *Studies in Surface Science and Catalysis,* **28**, 223-230.

Davis, M. E., & Lobo, R. F. 1992. Zeolite and molecular sieve synthesis. *Chemistry of Materials,* **4**(4), 756-768.

Degnan, T. F., Chitnis, G. K., & Schipper, P. H. 2000. History of ZSM-5 fluid catalytic cracking additive development at Mobil. *Microporous and Mesoporous Materials,* **35–36**(0), 245-252.

Dwyer, J., Karim, K., Smith, W., Thompson, N., Harris, R. K., & Apperley, D. C. 1991. A comparison of siliceous faujasitic zeolites produced by direct synthesis or by secondary synthesis. *The Journal of Physical Chemistry,* **95**(22), 8826-8831.

Egeblad, K., Christensen, C. H., Kustova, M., & Christensen, C. H. 2007. Templating Mesoporous Zeolites†. *Chemistry of Materials,* **20**(3), 946-960.

Falamaki, C., Edrissi, M., & Sohrabi, M. 1997. Studies on the Crystallization Kinetics of Zeolite ZSM-5 With 1,6-Hexanediol as a Structure-Directing Agent. *Zeolites,* **19**(1), 2-5.

Feng, H., Li, C., & Shan, H. 2009a. Effect of Calcination Temperature of Kaolin Microspheres on the In situ Synthesis of ZSM-5. *Catalysis Letters,* **129**(1-2), 71-78.

Feng, H., Li, C., & Shan, H. 2009b. In-situ synthesis and catalytic activity of ZSM-5 zeolite. *Applied Clay Science,* **42**(3–4), 439-445.

Friedman, H. 1991. Geiger counter spectrometer for industrial research. *Powder Diffraction,* **6**(03), 130-136.

Gougazeh, M., & Buhl, J. C. 2014. Synthesis and characterization of zeolite A by hydrothermal transformation of natural Jordanian kaolin. *Journal of the Association of Arab Universities for Basic and Applied Sciences,* **15**(0), 35-42.

Griffiths, P. R., & De Haseth, J. A. (2007). *Fourier transform infrared spectrometry* (Vol. 171): John Wiley & Sons.

Haag, W., Lago, R., & Weisz, P. 1984. The active site of acidic aluminosilicate catalysts.

Howell, P. A. (1963). Process for synthetic zeolite a: Google Patents.

International Zeolite Association. (2014). Database of Zeolite Structure. Retrieved 11/16/2014, from www.iza-online.org

Jacobs, P., Flanigen, E., Jansen, J., & van Bekkum, H. (2001). *Introduction to zeolite science and practice*: Elsevier.

Jenkins, R., & Snyder, R. L. (1996). Diffraction Theory *Introduction to X-ray Powder Diffractometry* (pp. 47-95): John Wiley & Sons, Inc.

Johnson, E. B. G., & Arshad, S. E. 2014. Hydrothermally synthesized zeolites based on kaolinite: A review. *Applied Clay Science,* **97–98**(0), 215-221.

Kacirek, H., & Lechert, H. 1976. Rates of crystallization and a model for the growth of sodium-Y zeolites. *The Journal of Physical Chemistry,* **80**(12), 1291-1296.

Kang, S.-J., Egashira, K., & Yoshida, A. 1998. Transformation of a low-grade Korean natural zeolite to high cation exchanger by hydrothermal reaction with or without fusion with sodium hydroxide. *Applied Clay Science,* **13**(2), 117-135.

Keil, F. J. 1999. Methanol-to-hydrocarbons: process technology. *Microporous and Mesoporous Materials,* **29**(1–2), 49-66.

Khatamian, M., & Irani, M. 2009. Preparation and characterization of nanosized ZSM-5 zeolite using kaolin and investigation of kaolin content, crystallization time and temperature changes on the size and crystallinity of products. *Journal of the Iranian Chemical Society,* **6**(1), 187-194.

Kliewer, C. (2009). Electron Microscopy and Imaging. In A. Chester & E. G. Derouane (Eds.), *Zeolite Characterization and Catalysis* (pp. 169-196): Springer Netherlands.

Konno, H., Tago, T., Nakasaka, Y., Ohnaka, R., Nishimura, J.-i., & Masuda, T. 2013. Effectiveness of nano-scale ZSM-5 zeolite and its deactivation mechanism on catalytic cracking of representative hydrocarbons of naphtha. *Microporous and Mesoporous Materials,* **175**(0), 25-33.

Kovo, A. S., Hernandez, O., & Holmes, S. M. 2009. Synthesis and characterization of zeolite Y and ZSM-5 from Nigerian Ahoko Kaolin using a novel, lower temperature, metakaolinization technique. *Journal of Materials Chemistry,* **19**(34), 6207-6212.

Kumar, N., Nieminen, V., Demirkan, K., Salmi, T., Yu. Murzin, D., & Laine, E. 2002. Effect of synthesis time and mode of stirring on physico-chemical and catalytic properties of ZSM-5 zeolite catalysts. *Applied Catalysis A: General,* **235**(1–2), 113-123.

Kwakye-Awuah, B., Von-Kiti, E., Buamah, R., Nkrumah, I., & Williams, C. 2014. Effect of Crystallization Time on the Hydrothermal Synthesis of Zeolites from Kaolin and Bauxite. *International Journal of Scientific and Engineering Research.*

Lancaster, M. (2010). *Green chemistry: An introductory text*: Royal society of chemistry.

LeGalley, D. P. 1935. A Type of Geiger - Müller Counter Suitable for the Measurement of Diffracted Mo K X - Rays. *Review of Scientific Instruments,* **6**(9), 279-283.

Linares, C. F., & Brikgi, M. 2006. Interaction between antimicrobial drugs and antacid based on cancrinite-type zeolite. *Microporous and Mesoporous Materials,* **96**(1–3), 141-148.

Linares, C. F., Solano, S., & Infante, G. 2004. The influence of hydrotalcite and cancrinite-type zeolite in acidic aspirin solutions. *Microporous and Mesoporous Materials,* **74**(1–3), 105-110.

Lowe, B. M. (1988). Synthesis Mechanisms for Zeolites and Molecular Sieves. In W. J. M. E. F. V. P.J. Grobet & G. Schulz-Ekloff (Eds.), *Studies in Surface Science and Catalysis* (Vol. Volume 37, pp. 1-12): Elsevier.

McAleer, A. M., Rees, L. V. C., & Nowak, A. K. 1991. Ion exchange and aluminum distributions in ZSM-5 zeolites. *Zeolites,* **11**(4), 329-336.

McCusker, L. B., & Baerlocher, C. (2005). Zeolite structures. In J. Čejka & H. v. Bekkum (Eds.), *Studies in Surface Science and Catalysis* (Vol. 157, pp. 41-64): Elsevier.

Mohamed, R. M., Aly, H. M., El-Shahat, M. F., & Ibrahim, I. A. 2005. Effect of the silica sources on the crystallinity of nanosized ZSM-5 zeolite. *Microporous and Mesoporous Materials,* **79**(1–3), 7-12.

Morris, R. E. 2010. Ionothermal synthesis of zeolites and other porous materials. *Zeolites and Catalysis: Synthesis, Reactions and Applications,* 87-105.

Moscou, L. 1991. The zeolite scene. *Studies in Surface Science and Catalysis,* **58,** 1-12.

Murat, M., Amokrane, A., Bastide, J., & Montanaro, L. 1992. Synthesis of zeolites from thermally activated kaolinite. Some observations on nucleation and growth. *Clay Minerals,* **27**(1), 119-130.

Nastro, A., Gabelica, Z., Bodart, P., & Nagy, J. B. (1984). Competitive Roles of Alkali and TPA Cations During Nucleation and Growth of ZSM-5 Zeolite. In S. Kaliaguine & A. Mahay (Eds.), *Studies in Surface Science and Catalysis* (Vol. Volume 19, pp. 131-137): Elsevier.

Ozin, G. A. 1992. Nanochemistry: synthesis in diminishing dimensions. *Advanced Materials,* **4**(10), 612-649.

Park, S.-E., & Jiang, N. (2010). Morphological Synthesis of Zeolites *Zeolites and Catalysis* (pp. 131-153): Wiley-VCH Verlag GmbH & Co. KGaA.

Pease, R., & Nixon, W. 1965. High resolution scanning electron microscopy. *Journal of Scientific Instruments,* **42**(2), 81.

Petrik, L. F., O'Connor, C. T., & Schwarz, S. (1995). The influence of various synthesis parameters on the morphology and crystalsize of ZSM-5 and the relationship between morphology and crystal size and propene oligomerization activity. In H. G. K. I. K. H.K. Beyer & J. B. Nagy (Eds.), *Studies in Surface Science and Catalysis* (Vol. Volume 94, pp. 517-524): Elsevier.

Prokof'ev, V. Y., & Gordina, N. E. 2014. Preparation of granulated LTA and SOD zeolites from mechanically activated mixtures of metakaolin and sodium hydroxide. *Applied Clay Science,* **101**(0), 44-51.

Reyes, C. A. R., Williams, C. D., & Alarcón, O. M. C. 2010. Synthesis of zeolite LTA from thermally treated kaolinite. *Revista Facultad de Ingeniería Universidad de Antioquia*(53), 30-41.

Rimoli, M. G., Rabaioli, M. R., Melisi, D., Curcio, A., Mondello, S., Mirabelli, R., & Abignente, E. 2008. Synthetic zeolites as a new tool for drug delivery. *J Biomed Mater Res A,* **87**(1), 156-164.

Ríos, C. A., Williams, C. D., & Fullen, M. A. 2009. Nucleation and growth history of zeolite LTA synthesized from kaolinite by two different methods. *Applied Clay Science,* **42**(3–4), 446-454.

Rivera, A., Farı, amp, x, as, T., Ruiz-Salvador, A. R., & de Ménorval, L. C. 2003. Preliminary characterization of drug support systems based on natural clinoptilolite. *Microporous and Mesoporous Materials,* **61**(1–3), 249-259.

Sebastián, V., Casado, C., & Coronas, J. (2010). Special Applications of Zeolites *Zeolites and Catalysis* (pp. 389-410): Wiley-VCH Verlag GmbH & Co. KGaA.

Shirazi, L., Jamshidi, E., & Ghasemi, M. 2008. The effect of Si/Al ratio of ZSM - 5 zeolite on its morphology, acidity and crystal size. *Crystal Research and Technology,* **43**(12), 1300-1306.

Smith, B. C. (2011). *Fundamentals of Fourier transform infrared spectroscopy*: CRC press.

Thomson, J. J. 1897. XL. Cathode Rays. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science,* **44**(269), 293-316.

Tosheva, L., & Valtchev, V. P. 2005. Nanozeolites: Synthesis, Crystallization Mechanism, and Applications. *Chemistry of Materials,* **17**(10), 2494-2513.

Tschernich, R. W. (1992). *Zeolites of the World*: Geoscience Press.

Van der Gaag, F. J. 1987. ZSM-5 type zeolites: Synthesis and use in gasphase reactions with ammonia.

Von Ardenne, M. 1938. Das Elektronen-Rastermikroskop. *Zeitschrift für Physik,* **109**(9-10), 553-572.

Ward, J. W. 1967. The nature of active sites on zeolites: I. The decationated Y zeolite. *Journal of Catalysis,* **9**(3), 225-236.

Win, P. P. 2004. Preparation of Synthetic Zeolites From Myanmar Clay Mineral.

Wischnitzer, S. (1981). *Introduction to Electron Microscopy*: Pergamon Press.

Wong, L. W. (2006). *Molecular delivery system based on the nanoporous zeolite microstructure.* (Doctoral thesis), Hong Kong University of Science and Technology.

Wright, P. A., & Pearce, G. M. (2010). Structural Chemistry of Zeolites *Zeolites and Catalysis* (pp. 171-207): Wiley-VCH Verlag GmbH & Co. KGaA.

Xu, R., Pang, W., Yu, J., Huo, Q., & Chen, J. (2009). *Chemistry of zeolites and related porous materials: synthesis and structure*: John Wiley & Sons.

Xu, R. R., Gao, Z., & Xu, Y. (1995). *Progress in Zeolite Science: A China Perspective*: World Scientific.

Yang, S., Lach-Hab, M., Vaisman, I. I., Blaisten-Barojas, E., Li, X., & Karen, V. L. 2010. Framework-type determination for zeolite structures in the inorganic crystal structure database. *Journal of Physical and Chemical Reference Data,* **39**(3), 033102.

Ye, L., Xianbo, Y., Lei, Q., Jingdai, W., & Yongrong, Y. 2010. In-situ synthesis of ZSM-5 zeolite from metakaolin/spinel and its catalytic performance on methanol conversion. *China Petroleum Processing & Petrochemical Technology,* **12**(1), 23-28.

Yu, J. (2007). Chapter 3 Synthesis of zeolites. In H. v. B. A. C. Jiří Čejka & S. Ferdi (Eds.), *Studies in Surface Science and Catalysis* (Vol. Volume 168, pp. 39-103): Elsevier.

Zhang, Y., Gao, W., & Cui, L. (2007). The transformation of acid leached metakaolin to zeolite beta. In Z. G. J. C. Ruren Xu & Y. Wenfu (Eds.), *Studies in Surface Science and Catalysis* (Vol. Volume 170, pp. 420-425): Elsevier.