MORDENITE ZEOLITES SYNTHESIZED FROM BAMBOO LEAVES ASH FOR ACETYLATION OF GLYCEROL WITH BENZALDEHYDE

GONG JIANGTIAN

UNIVERSITI SAINS MALAYSIA

2025

MORDENITE ZEOLITES SYNTHESIZED FROM BAMBOO LEAVES ASH FOR ACETYLATION OF GLYCEROL WITH BENZALDEHYDE

by

GONG JIANGTIAN

Thesis submitted in fulfilment of the requirements
for the degree of
Master of Science

August 2025

ACKNOWLEDGEMENT

Special appreciation goes to my supervisor, Assoc. Prof. Dr. Ng Eng Poh, for his guidance, inspiration, devotion, patience, and perpetual encouragement throughout this research.

I am deeply thankful to School of Chemical Sciences, Universiti Sains Malaysia (USM) for offering me an opportunity to pursue MSc at Chemistry with sufficient research facilities, great supports from administrative, academic and technical staff.

I would like to thank to express special gratitude to my beloved parents for their unconditional support, motivation, and encouragement. It is impossible for me to finish this work without their encouragement and understanding.

Lastly, I would like to give my heartfelt thanks to my friends for helping me the relevant and useful information in the process of completing this project.

TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF SYMBOLS AND NOMENCLATURES

℃	Degree Celsius
Al	Aluminum
Å	Angstrom (1×10^{-10} m)
Al_2O_3	Aluminum oxide
$Al(OH)_3$	Aluminum hydroxide
$Al_2(SO_4)_3$	Aluminum sulfate
CH_3COOH	Acetic acid
HCl	Hydrochloric acid
HNO_3	Nitric acid
H_2SO_4	Sulfuric acid
KBr	Potassium bromide
Na^+	Sodium ion
NaOH	Sodium hydroxide
NH_4Cl	Ammonium chloride
nm	Nanometer (1×10^{-9} m)
Si	Silicon
SiO_2	Silicon dioxide

LIST OF ABBREVIATIONS

BET	Brunauer-Emmet-Teller
BLA	Bamboo leaf ash
D_{av}	Average pore size from BJH adsorption curve
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
GC-FID	Gas chromatography with flame ionization detection
GC-MS	Gas chromatography mass spectrometry
h	Hour(s)
IUPAC	International Union of Pure and Applied Chemistry
IZA-SC	Structure Commission of the International Zeolite Association
MAS NMR	Magic angle spinning unclear magnetic resonance spectroscopy
mg	Milligram
min	Minute(s)
OTMS	Octadecyltrimethoxysilane
S_{BET}	Total surface area
S_{micro}	Micropore surface area
S_{ext}	External surface area
TG/DTG	Thermogravimetric and differential thermal analysis
TOF	Turnover frequency
TON	Turnover number
TPD	Temperature-programmed desorption
XRD	X-ray diffraction
XRF	X-ray fluorescence

V_{meso}	Mesopore volume
V_{Tot}	Total pore volume

LIST OF APPENDICES

SINTESIS ZEOLIT MORDENIT DARIPADA ABU DAUN BULUH UNTUK PENGASITILAN GLISEROL DENGAN BENZALDEHID

ABSTRAK

Abu daun buluh (BLA) adalah sumber silika yang murah dan lestari tetapi kurang digunakan dalam industri. Setiap tahun, lebih daripada 20 juta tan buluh dituai di seluruh dunia dengan menghasilkan kira-kira 200,000 tan sisa daun yang sering dilupuskan melalui pembakaran terbuka. Dengan menggunakan semula sisa ini ianya dapat menawarkan penyelesaian yang mesra alam terhadap masalah alam sekitar. Dalam kerja ini, zeolit mordenit dan mordenit berstruktur hierarki yang disintesis daripada BLA telah dilapor. Dengan mengkaji keadaan penghabluran dengan teliti, mordenit dengan tiga morfologi yang berbeza (nanobatang, bebola besar antartumbuh, nanorod) berjaya disintesis. Mordenit dengan bentuk nanorod mengandungi mikro/mesoliang berstruktur hierarki, dan merupakan mangkin terbaik (80.2±2.4% penukaran, 54.4±0.3% kepilihan terhadap dioksolana) berbanding mangkin mordenit yang disediakan dalam pengasetilan benzaldehid dan gliserol. Prestasi pemangkinannya adalah lebih baik daripada mangkin homogen tradisional dan zeolit dalam keadaan optimum (muatan mangkin = 0.100 g, nisbah molar benzaldehid:gliserol = 7:1, suhu = 180 ℃, masa = 10 min) dengan kebolehgunaan semula yang tinggi (penukaran 80.2±2.4% → 74.4±1.3% selepas kitaran ke-5). Sementara itu, mordenit hierarki dengan mikro/mesoliang (TM-n) juga disintesis menggunakan kaedah acuan lembut dengan mempelbagaikan amaun oktadesiltrimetoksisilana (nisbah OTMS/Al_2O_3, n = 0.2, 0.3 dan 0.4) dalam hidrogel.

OTMS bukan saja menghasilkan mesoliang sekunder dalam kerangka zeolit, malah juga mempengaruhi proses penghabluran, morfologi, kehabluran dan nisbah Si/Al. Mordenit hierarki TM-0.3 mengandungi jumlah OTMS optimum, dan antartumbuh ANA/GIS terbentuk jika jumlah OTMS ditingkatkan lagi. Dengan keliangan hierarki yang boleh diakses, keasidan yang berkurangan dan kesan morfologi, sampel TM-0.3 mempamerkan prestasi pemangkinan yang sangat baik (penukaran 84.1±2.1%, 61.5±0.4% kepilihan terhadap dioksolana) dalam pengasetilan gliserol dan benzaldehid (160 ℃, 20 min) dan lebih baik daripada mordenit asal dan mangkin lain dalam keadaan optimum (muatan mangkin = 0.050 g, nisbah molar benzaldehid:gliserol = 7:1).

MORDENITE ZEOLITES SYNTHESIZED FROM BAMBOO LEAVES ASH FOR ACETYLATION OF GIYCEROL WITH BENZALDEHYDE

ABSTRACT

Bamboo leaves ash (BLA) is a cheap and sustainable silica source but under-utilized in industry. Annually, over 20 million tons of bamboo are harvested worldwide, generating about 200,000 tons of leaves waste often disposed of by open burning. Valorizing this waste hence offers an eco-friendly solution to environmental problems. In this work, mordenite and hierarchical mordenite zeolites synthesized from BLA are reported. By carefully studying crystallization conditions, mordenites with three distinct morphologies (nanostick, intergrown bulky ball, nanorod) are successfully synthesized. The mordenite with nanorod shape contains hierarchical micro/mesoporosity, and is the best catalyst (80.2±2.4% conversion, 54.4±0.3% dioxolane selectivity) among mordenite catalysts prepared in acetalization of benzaldehyde and glycerol. Its catalytic performance under optimum conditions (catalyst loading = 0.100 g, benzaldehyde:glycerol molar ratio = 7:1, temperature = 180 ℃, tine = 10 min) is even better than those of classical homogeneous and zeolite catalysts with high recyclability (80.2±2.4% → 74.4±1.3% conversion after 5th cycle). Meanwhile, hierarchical mordenites with micro/mesoporosity (TM-*n*) are also synthesized using soft-templating approach by varying octadecyltrimethoxysilane amount (OTMS/Al_2O_3 ratio, *n* = 0.2, 0.3 and 0.4) in hydrogels. OTMS not only creates secondary mesoporosity in zeolite framework, but also influences the crystallization process, morphology, crystallinity and Si/Al ratios. TM-0.3

hierarchical mordenite has the optimum OTMS amount incorporated while further increasing the OTMS amount leads to the formation of ANA/GIS intergrowth. By having accessible hierarchical porosity, reduced acidity and morphological effects, TM-0.3 sample exhibits excellent catalytic performance (84.1±2.1% conversion, 61.5±0.4% dioxolane selectivity) in acetylation of glycerol and benzaldehyde (160 ℃, 20 min) better than pristine mordenite (MOR-3) and other catalysts under optimum reaction conditions (catalyst loading = 0.050 g, benzaldehyde:glycerol molar ratio = 7:1).

CHAPTER 1

INTRODUCTION

1.1 General introduction

Zeolites are aluminosilicate crystalline microporous solids widely used as catalysts, ion exchangers, and adsorbents due to their high surface area, uniform pore sizes, and exchangeable cations (Bajec et al., 2023; Chu et al., 2023; Shi et al., 2023; Hanh et al., 2024). Among the 251 types of zeolites known today, mordenite is notable for its two-dimensional large pore channels (7.0 × 6.5 $Å^2$), which make it highly effective in separation and catalytic applications (Xu et al., 2012). Additionally, mordenite exhibits exceptional thermal and chemical stability, making it a robust zeolite suitable for use in harsh reaction environments (Shaikh et al., 1993).

Traditionally, mordenite can be synthesized using hydrothermal methods with appropriate aluminum sources (e.g. $Al_2(SO_4)_3$ (Bajpai et al., 1978), $NaAlO_2$ (Nada et al., 2019)), and silica sources (e.g. silica gel (Zhu et al., 2017), fumed silica (Abdelrahman et al., 2020), either in the absence (Chen et al., 2019) or presence of organic templates (e.g., tetraethylammonium hydroxide (Nada et al., 2019), piperazine (Zhang et al., 2015), or $C_{16}H_{33}$-[N^+-methylpyrrolidine] (Bai et al., 2019)). The choice of different Al and Si sources, as well as organic templates, allows tailoring of the resulting zeolite crystals to desired sizes, morphologies, and functionalities suited for specific applications (Bai et al., 2019; Bolshakov et al., 2019).

Recently, increasing awareness of environmental issues has motivated researchers to seek alternative and sustainable silica sources for zeolite synthesis (Rilyanti et al., 2016). Amorphous silica derived from agricultural waste such as rice husk, cogon grass, bamboo leaves, and sugarcane bagasse has been utilized to synthesize various types of zeolites (Wong et al., 2017; Bunmai et al., 2018; Abdul Rahman et al., 2019). Bamboo leaves ash (BLA) has been reported as an eco-friendly silica source for crystallizing zeolites such as LTA (Ng et al., 2017), MER (Cheong et al., 2020), and FAU-X (Ng et al., 2017). BLA is considered economical and abundant in Asia, with the plant containing up to 40% silica (Putranto et al., 2021). Annually, the worldwide bamboo harvest exceeds 20 million tons, producing approximately 200,000 tons of bamboo leaves as waste, typically disposed of by open burning (Emamverdian et al., 2020). Utilizing and valorizing this agricultural waste offers an environmentally friendly approach to addressing ecological concerns.

Furthermore, the transesterification of vegetable oils or animal fats with methanol produces biodiesel as the primary product, along with a glycerol-rich byproduct (~100 kg per tonne of biodiesel) (Kowalska-Kus et al., 2017). This byproduct contains residual glycerol, spent catalysts, and excess methanol. As global biodiesel production grows, the surplus glycerol presents increasing utilization challenges, necessitating innovative valorization strategies to convert this low-value waste into high-value chemical feedstocks. Glycerol acetalization has emerged as a promising avenue for such valorization.

1.2 Problem Statement

The utilization of sustainable and environmentally friendly silica sources is crucial in the synthesis of zeolites to reduce pollution and dependence on non-renewable resources. However, conventional silica materials such as quartz and sand require costly and environmentally unfriendly processing methods (Abdul Razak et al., 2022). Therefore, the search for alternative, inexpensive, abundant, and sustainable silica sources has become an urgent necessity.

One promising candidate is bamboo leaf ash (BLA), a waste product from bamboo agriculture that is widespread in Asia. Although BLA contains a high silica content, its application in zeolite synthesis remains underdeveloped. It faces challenges related to controlling the production processes and achieving the desired material properties.

Furthermore, there is a need to enhance catalytic efficiency in producing high-value chemicals, such as glycerol and benzaldehyde acetalization, which are related to glycerol waste from biodiesel production and environmentally friendly chemical manufacturing. The use of zeolite catalysts derived from this sustainable silica source could address these issues, but comprehensive studies on their synthesis, characterization, and catalytic performance are still limited, thus forming the basis of this work.

1.3 Research objectives

a. To synthesize mordenite and hierarchical mordenite zeolites using bamboo leaves silica ash under hydrothermal conditions.

b. To characterize the physico-properties (crystal structure, porosity, surface acidity) of mordenite and hierarchical mordenite zeolites.

d. To study the catalytic behavior of mordenite zeolites in acetalization of benzaldehyde and glycerol using non-microwave instant heating.

1.4 Scope of study

The scope of this study is focused on the synthesis and characterization of mordenite and hierarchical mordenite zeolites using agricultural waste, specifically bamboo leaves ash, as a sustainable silica source. The research first investigates the effects of various hydrothermal synthesis parameters, such as SiO2, Na2O and water content, on the formation of mordenite. Additionally, the study explores the development of hierarchical structures by incorporating octadecyltrimethoxysilane (OTMS) as a mesoporogen to enhance pore accessibility. The physicochemical properties of the synthesized zeolites are thoroughly characterized using techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and solid-state NMR spectroscopy, and so on. Furthermore, the catalytic performance of these zeolites is evaluated in the acetalization reactions of benzaldehyde and glycerol under non-microwave instant heating conditions. The study aims to utilize agricultural waste as an environmentally sustainable silica source and focuses on the

hydrothermal synthesis method. It emphasizes investigating how various synthesis parameters affect the structural characteristics and catalytic performance of the resulting zeolites. Ultimately, this research seeks to provide valuable insights into eco-friendly zeolite production and explore their potential applications in catalysis.

1.5 Overview of the thesis

This thesis is composed of six chapters that cover the background, literature study, experimental procedures and research findings of the project.

Chapter 1 is an introduction dedicating to the general introduction, definition, properties and applications of zeolite. The problem statements, objectives and overview of this work are also covered in this chapter too.

Chapter 2 is a comprehensive literature review describing zeolites, mordenite framework structure and its properties, the zeolite synthesis methods and their applications. In addition, a description about the characterization techniques used in this study is also mentioned in this chapter.

Chapter 3 presents the experimental methodology used in this study where the synthesis conditions of microporous mordenite and hierarchical micro/mesoporous mordenite zeolites using hydrothermal method are detailed. In addition, the instruments used in sample characterization are described in this chapter. Furthermore, the protocol for carrying out catalytic acetalization of benzaldehyde and glycerol under non-microwave instant heating condition is also described in this chapter.

Chapter 4 presents the results of synthesis and formation study of mordenite zeolite from bamboo leaves ash under hydrothermal condition. Then, the effects of synthesis parameters, such as silicon, sodium and water contents on crystallization of mordenite zeolite are studied. The study is followed by investigating the catalytic performance of mordenite zeolite in acetalization of benzaldehyde and glycerol using non-microwave instant heating.

Chapter 5 reports the findings of soft-templating octadecyltrimethoxysilane (OTMS) synthesis of hierarchical mordenite where the effects of OTMS content on the physicochemical and catalytic properties of hierarchical mordenite are studied. For the analysis of sample characterization in this chapter, in addition to the techniques mentioned in Chapter 4, ^{29}Si MAS NMR spectra was used to analyze the samples. Furthermore, comparative catalytic performance with classical homogeneous and heterogeneous catalysts, including H_2SO_4, HCl, CH_3COOH, H-Y, H-LTL, Na-X and Na-A, is also studied.

Chapter 6 concludes the research findings. Furthermore, the recommendations for the future work of this research are also given at the end of this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Zeolites

Zeolites are crystalline aluminosilicate solids with uniform microporosity (<0.2 nm). The first zeolite mineral stilbite was first discovered by a mineralogist, Axel Fredrik Cronstedt, in 1756 (Colella and Gualtieri, 2007). Nowadays, zeolites are widely used in various industries as catalysts, ion exchangers, molecular sieves and adsorbents due to their high surface area with uniform pore sizes and defined shapes besides having exchangeable cations (Pérez-Botella et al., 2022). The pore size and shape of zeolites can be adjusted to enable the selective adsorption and catalysis of different molecules (Vansant, 1988). Also, the chemical composition of zeolites can also be altered by introducing different metal ions or organic groups that further modify their surface acidity, electrical and hydrophobic properties (Anpo et al., 2000).

Zeolites can be found naturally in various geological places, such as volcanic ashes, saline lake deposits, and other open cavities in volcanic rocks, etc. (Colella and Gualtieri, 2007). In addition, zeolites can also be synthesized in the laboratory. The main techniques to synthesize zeolites are the hydrothermal method, solvothermal method, organic template method, etc. The hydrothermal method is the most used technique which employs water as the reaction medium at high temperature and pressure. It involves mixing and reacting silica, alumina and alkali mineralizer to crystallize zeolites at a specific temperature and duration (Busca, 2020).

The templating method employs organic molecules or polymers as structure-directing agents to control the pore structure and morphology of zeolites. During the synthesis, the template molecules are confined in the zeolite framework, and they are removed *via* calcination after the synthesis to open the pores of zeolites. So far, there are more than 160 types of zeolite frameworks that have successfully been identified and synthesized (IZA-SC).

2.2 Mordenite

Mordenite is one of the most famous zeolites and it is one of the six most common zeolites of commercial interest. It was first described in 1864 by Henry How, who named it after the town of Morden on the Bay of Fundy coast in Nova Scotia, Canada (IZA-SC). Mordenite can be found as natural rocks at volcanic sediments and marine sediments. Also, it can be synthesized in the laboratory where the crystal morphologies can be massive, textured needles, fibrous polymers or small prisms (Narayanan et al., 2021).

Mordenite exhibits the MOR topology, and it has a two-dimensional pore channel system made up of 12-membered ring (Figure. 2.1) (IZA-SC, 2025). Mordenite has a high Si/Al ratio ranging (Gili and Conato, 2019), making it more thermally stable and resistant to acid corrosion than other zeolites. Besides, it has large pore opening (0.65 nm), allowing it a very famous zeolite used in many applications.

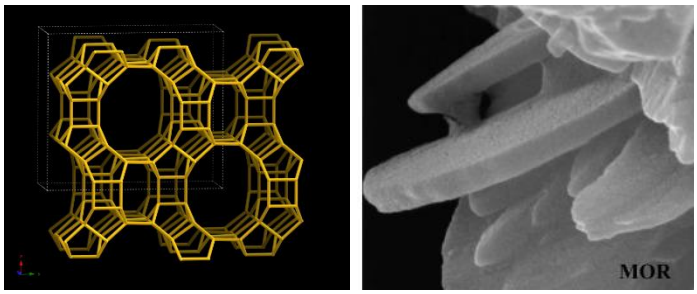

Figure 2.1 (a) Framework structure and (b) SEM image of MOR zeolite. (Fallah and Sohrabnezhad, 2019).

Mordenite zeolite is typically synthesized through hydrothermal method where organic templating agents are often used to direct the crystallization. Organic templating agents can enhance the crystallinity and purity of mordenite but the use of organic templates also increases the production costs besides causing environmental pollution. Some organic templates that have been used for crystallizing mordenite zeolite are polyethylene glycol (PEG) (Liu et al., 2016), cetrimonium bromide (CTAB) (Jin et al., 2011, Liu et al., 2016) and tetraethylammonium hydroxide (TEAOH) (Jin et al., 2011). Therefore, several studies on template-free and low-cost templating synthesis of mordenite zeolite have been explored.

In addition, a method for the synthesis of serpentine without templating agents is reported. Mordenite zeolite with crystal diameter 65 nm and crystal length 7 μm was successively synthesized in the absence of organic template by hydrothermal method at 180 ℃ for 5 days after stirring at high speed and aging in the synthesis mixture with the molar composition of $12Na_2O:100SiO_2:2Al_2O_3:500H_2O$ (Aly et al., 2012).

The synthesis conditions of mordenite are also influenced by the silicon and aluminum sources. Some research has employed different silicon and aluminum sources, such as rice husk ash (Bajpai et al., 1981), metakaolin (Aono et al., 2018, Klunk et al., 2020) as substitutes for commercially sourced sodium silicate and sodium aluminate. These alternative sources not only reduce the synthesis costs but also make use of waste materials which further reduce the environmental impact.

In 1978, Bajpai et al. reported the successful synthesis of partially pure mordenite (MOR) zeolite at 135−165 °C by using semi-dissolved rice husk silica ash. The preparation work is considerably tedious and not industrially practical because the silica ash extracted solutions for every batch has different silica and sodium contents, and hence quantification is needed before using in zeolite synthesis.

In 2020, Klunk et al. used RHA and metakaolin as silica and alumina sources, respectively, for crystallizing MOR zeolite. The average cation-exchange capacity values varied between 1.10 and 1.78 meq/g, demonstrating a 62% improvement for mordenite prepared with $0.41SiO_2$:$0.22Al_2O_3$:11.19NaOH:$27.78H_2O$ over mordenite prepared with $0.23SiO_2$:$0.12Al_2O_3$:11.19NaOH:$27.78H_2O$. This outcome holds promise for the application of mordenite as an ion exchanger and adsorbent (Klunk et al., 2020). Nevertheless, the resulting products are still contaminated with kaolinite, mullite and quartz.

In 2023, Lankapati et al. used fly ash as silica and alumina sources for crystallizing MOR zeolite. It was found that zeolites synthesized with varying the molar ratios of Al_2O_3 from waste coal fly ash (CFA) shows significant potential as

solid acid catalysts for the esterification of levulinic acid to produce n-butyl levulinate. Reducing the content of Al_2O_3 enhances the acidity of the zeolitic materials, thereby improving their catalytic activity. Furthermore, using the CFA waste for zeolite synthesis also substantially reduces the overall cost of zeolite production (Lankapati et al., 2023).

The crystallization process of mordenite is a complex reaction since it is influenced by various reaction conditions, including silica and aluminum contents, temperature, pressure, time, pH value, water amount, stirring speed, etc. (Wang et al., 2021). These conditions not only affect the crystal growth, morphology and size but also the surface hydrophilicity (Si/Al ratio) (Aly et al., 2012). For instance, Mignoni et al. use kaolin as silica and alumina sources for synthesizing mordenite zeolite (Mignoni et al., 2008). The effects of crystallization time and seed addition were then studied. The results showed that kaolin is an ideal silica and alumina sources for the synthesis of mordenite where an addition of mordenite zeolite seeds resulted in fast crystallization with higher crystallinity.

2.3 Amorphous silica sources from agricultural waste

Agricultural wastes are plant residues from agriculture. These wastes are not used as food for humans or animals. Amorphous silica from agricultural wastes, such as rice husk, cogon grass, bamboo leaves and sugarcane bagasse, have recently been used for synthesizing various types of zeolites (Wong et al., 2017, Wong et al., 2017, Bunmai et al., 2018, Abdul Rahman et al., 2019). The amorphous silica ashes are usually obtained through acid treatment, followed by combustion. Particularly,

bamboo leaves ash (BLA) has been reported as a green silica source for crystallizing Linde Type A (LTA) (Ng et al., 2017), Merlinoite (MER) (Cheong et al., 2020) and Faujasite-X (FAU-X) zeolites (Ng et al., 2017) because it is economical, abundant in Asia and the plant contains the highest silica content (40%) (Putranto et al., 2021). Annually, the worldwide bamboo harvest surpasses 20 million tons, producing ~200,000 tons of bamboo leaves as waste, which are usually disposed *via* open burning (Emamverdian et al., 2020). Hence, using and valorizing this agricultural waste offer an eco-friendly approach to addressing these environmental issues.

2.4 Synthesis methods of zeolites

2.4.1 Hydrothermal synthesis

Hydrothermal and solvothermal synthesis are popular synthesis methods for zeolite synthesis. Hydrothermal synthesis is a synthesis method where a reaction medium is heated under high temperature and pressure, which can produce inorganic materials that are difficult to synthesize at low temperature and ambient pressure. The advantage of hydrothermal synthesis lies in its ability to mimic natural geothermal process for crystallizing natural zeolites. To allow the synthesis to be conducted at high temperature and pressure, Teflon-lined stainless-steel autoclave is used (Figure. 2.2). The Teflon lining within the stainless-steel autoclave is very inert. So, it is to ensure excellent corrosion resistance, preventing the reaction vessel from being affected by the harsh chemical conditions (very low pH or very high pH) at high temperature and pressure.

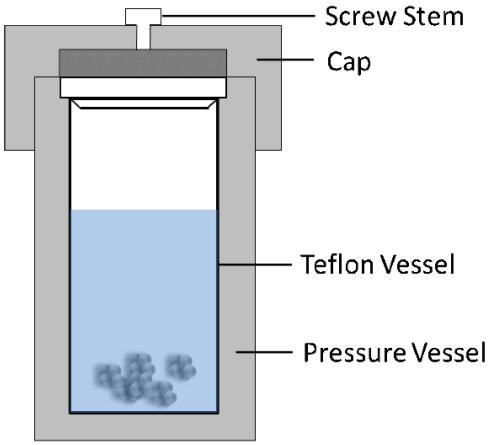

Figure 2.2 Teflon-lined autoclave.

So far, many types of zeolites have been synthesized using hydrothermal method, namely zeolite P (Tamura et al., 2006), NaY (Katsuki et al., 2001), ZSM-5 (Katsuki et al., 2005), etc. During hydrothermal synthesis, the zeolite synthesis involves two stages, namely dissolution and crystallization. In the dissolution stage, the silicon and aluminum precursors undergo partial dissolution in the high-temperature, high-pressure aqueous solution, forming a supersaturated solution media. Then, the Si and Al precursors will react with each other through polycondensation and polymerization by connecting through Si and Al tetrahedral units, forming zeolite crystal structures (Brinker, 1988). In some cases, organic templates are added to direct the formation of a zeolite with specific pore structure. When the crystallization completes, the hydrothermal process is stopped by cooling it down to room temperature before the resulting zeolite product is washed and dried.

Extreme high temperature for hydrothermal synthesis is not advisable for zeolite synthesis. It is because it can lead to dense phase transformation since zeolites are metastable porous materials. In addition, appropriate heating time is another

crucial factor influencing the crystal growth, crystal size and crystallinity of zeolites. Excessively long heating time results in crystal agglomeration and dense phase transformation (Salahudeen, 2022). Therefore, the choice of reaction temperature and time are important for hydrothermal synthesis.

2.4.2 Microwave synthesis

Microwave synthesis is a chemical synthesis method that utilizes microwave radiation as an energy source (Li et al., 2019). It offers advantages such as rapid heating, uniform temperature distribution, low energy consumption, high selectivity and high yields (Kurian et al., 2022). As a result, microwave synthesis is very widely used in organic (Al-Etaibi and El-Apasery, 2022) and inorganic syntheses (Zhao and Yan, 2011).

Microwave is a type of electromagnetic wave with wavelengths ranging from 1 mm to 1 m and frequencies between 300 MHz and 300 GHz (Galema, 1997). The principle of microwave synthesis involves the polarization and rotation of polar molecules or ions in the material due to the action of microwave radiation, leading to interaction with the electric or magnetic fields of the microwaves (Figure. 2.3).

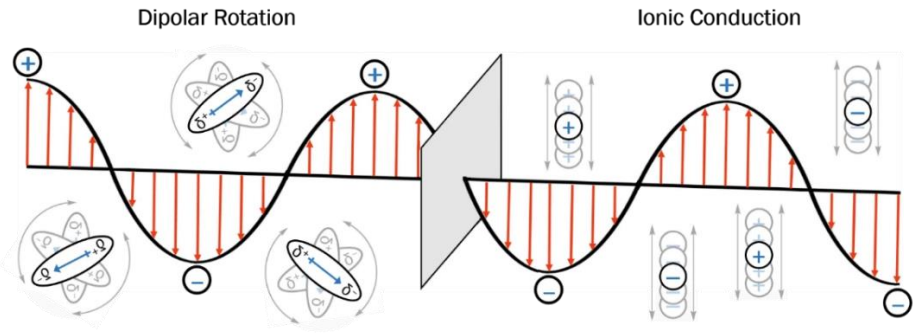

Figure 2.3 Mechanisms of microwave heating: dipolar rotation and ionic conduction. (CEM Corporation, 2025)

Recently, microwave energy is used in the synthesis of zeolites. For example, Julbe et al. synthesized MFI zeolite by using microwave (MW) heating to accelerate the secondary growth of MFI zeolite for making zeolite membranes (Julbe et al., 2005). Zeolite seeds (50-60 nm) were first prepared from fresh soils by microwave-assisted hydrothermal synthesis. The resulting MFI zeolite membrane has a thickness ranged from 200 nm to a few micrometers depending on the synthesis conditions.

In 2000, Xu et al. successfully synthesized NaA zeolite membranes on porous α-Al_2O_3 support by microwave heating (Xu et al., 2000). The synthesis of NaA zeolite membrane in microwave field took only 15 min, which is 10 times shorter than that of conventional heating. Scanning electron microscopy characterization and gas permeation studies showed that the zeolite NaA crystals in the membrane synthesized using microwave heating were uniform in size. The thickness of the membrane was about 4 μm, which was thinner than that of the NaA zeolite membrane synthesized by conventional heating (5-8 μm).

Furthermore, Ng et al. synthesized colloid stable nanoscale AlPO-5 crystals (ca. 300 nm) using microwave-assisted hydrothermal method templated by 1-ethyl-2,3-dimethylimidazolium hydroxide ([edmim]OH) template (Ng et al., 2014). The results show that [edmim]OH has a template effect on AlPO-5 nanocrystals. Under the effect of microwave energy, nanosized AlPO-5 crystals with high crystallinity and high porosity were produced. In addition, the AlPO-5 nanocrystals showed interesting morphologies due to the microwave energy and the unique structure-directing properties of $[edmim]^+$. It was also found that the microwave-prepared AlPO-5 nanocrystals had a higher water absorption capacity than those prepared by the hydrothermal method.

2.4.3 Ionothermal synthesis

Ionothermal synthesis has been widely used for the preparation of aluminophosphate-based molecular sieves, metal-organic frameworks, and covalent organic frameworks (Wu et al., 2019). In this technique, it uses ionic liquids simultaneously as both the solvent and template for the formation of zeolite materials (Morris, 2009).

In 2019, Wu et al. have been synthesized MTT, TON, ITW, and MFI zeolite under ionothermal condition (Wu et al., 2019). They added N,N′-diisopropylimidazolium iodide, NH_4F, SiO_2, H_2O and zeolite seeds on the mortar and mixed well. Then, the mixture was transferred to an autoclave for

crystallization. It was found that the key to crystallize the silica-based zeolites is the effective dissolution of silica in the ionic liquid.

In 2018, Azim and Moshin had successfully synthesized silicoaluminophosphate (SAPO) with LTA frameworks using ionothermal synthesis technique. In this work, 1-butyl-3-methylimidazolium bromide ([C_4mim]Br) as both a solvent and a structure-directing agent (SDA) was added, while tetramethylammonium fluoride ([Me_4N]F) was added as both a mineralizing agent and an auxiliary structure-directing agent. The presented ionothermal synthesis has shown to be more efficient than the conventional hydrothermal synthesis for crystallizing SAPO-LTA with higher crystallinity and uniform crystal size.

2.4.4 Sonothermal synthesis

Sonothermal synthesis is a new method for synthesizing zeolites where ultrasonic wave is used (Baig and Varma, 2012). In liquid media, high frequencies lead to different pressure sections and results in arising gas bubbles with constant growth until they collapse. This cavitation leads in locally high temperatures (1000–5000 K), high pressures (100–50000 bar), and fast heating/cooling ranges of 10^{10} K s^{-1} (Suslick, 1989).

In 2017, Hovestadt et al. reported a new synthetic route to the zeolitic imidazolate framework ZIF-4 (Hovestadt et al., 2017). The sonication was realized with a 200 W ultrasonicator. It was found that this new synthesis pathway for ZIF-4 allows simple and economical preparation of large quantity of ZIF-4 due to the

substantial reduced in the amount of dimethylamide used. In addition, the synthesis is almost five times faster compared to the conventional hydrothermal synthesis method.

2.4.5 Mechanochemical synthesis

Mechanochemical synthesis is the combination of mechanical and chemical methods to synthesize zeolites. Mechanochemical synthesis has advantages over traditional hydrothermal synthesis in some cases because use of this synthesis technique eliminates formation of a liquid phase (Gordina et al., 2003).

In 2003, Gordina et al. synthesized NaA zeolite by using mechanochemical synthesis method where hydrated aluminum, silica and sodium silicate were used as alumina and silica sources (Gordina et al., 2003). The milling synthesis was performed for 30 min in a VM-4 roller vibrating mill with a vibration frequency of 930 min^{-1}. It was found that the samples synthesized was a pure NaA zeolite but the resulting crystals have defective crystal structures.

In 2007, Garc et al. synthesized MFI-type titanosilicate zeolite TS-1 by a newly developed mechanochemical route and investigated the effect of mechanochemical reaction conditions on its physical and chemical properties (Garc et al., 2007). The results showed that the use of smaller starting material particles and dense grinding media can effectively mix titanium dioxide and silica. Longer grinding times and faster disc rotation speeds can greatly facilitate the mechanochemical reaction between titanium dioxide and silica. However, too long a grinding time or too fast a disc rotation speed can increase the amount of impurity zirconia produced

from the grinding jar and balls, which prevents nucleation of the FI phase and reduces the catalytic activity of the TS-1 material.

Table 2.1 summarizes all the commonly used methods for synthesizing zeolites, highlighting their key features along with their respective pros and cons to provide a comprehensive understanding of their applicability in different contexts.

Table 2.1 Synthesis methods of zeolites

Synthesis method	Description	Pros	Cons	References
Hydrothermal method	Crystallization in water at high temperature and pressure, reacting silica, alumina, and mineralizers.	Well-established, allows for controlled crystal size and shape.	Time-consuming, requires high energy input and pressure.	Busca, 2020, Sajjadi et al., 2020
Microwave method	Uses microwave radiation to accelerate crystallization processes.	Rapid synthesis, energy-efficient, reduced reaction times.	Equipment cost higher, scale-up challenges, possible uneven heating.	Peng et al., 2019, Yousefi et al., 2020
Ionothermal method	Uses ionic liquids instead of water as reaction media at moderate temperatures.	Environmentally friendly, enables unique zeolite phases.	Ionic liquids can be expensive, process control is complex.	Gunter et al., 2020, Chen et al., 2021
Sonothermal method	Employs ultrasonic waves to facilitate nucleation and growth.	Shorter synthesis times, improved crystallinity, energy efficient.	Limited scalability, equipment needed for ultrasonication.	Chen et al., 2019, Zhang et al., 2021
Mechanochemical method	Grinding or milling of raw materials to induce crystallization with minimal or no solvent.	Solvent-free, eco-friendly, reduces energy consumption, fast.	Less control over crystal size, often yields amorphous or mixed phases.	Wang et al., 2018, García et al., 2020

2.5 Characterization techniques

2.5.1 X-ray power diffraction (XRD)

X-ray Diffraction (XRD) is a very important characterization technique in zeolite research. It can be used to determine the crystalline phase, purity, crystallite size crystal orientation and chemical composition of zeolites (Schlögl, 2009). The XRD operates based on Bragg's Law, which states that when X-rays reflect off crystal planes within a material, constructive interference occurs if the following Equation 2.1 is satisfied:

$$n\lambda=2d\sin\theta \qquad \text{(Equation 2.1)}$$

where n is an integer, λ is the X-ray wavelength, d is the interplanar spacing and θ is the angle between the incident X-ray beam and the crystal plane (Figure. 2.4).

The X-ray detector collects the signals from the diffracted X-rays according to the intensity and converts them into diffraction patterns presented in intensity versus angle (2θ) (Brügemann and Gerndt, 2004). By measuring the position and intensity of these peaks at different θ angles, one can deduce the interplanar spacing and relative intensity of crystal planes, allowing inference of the crystal structure and phase composition of the material (Khan et al., 2020).

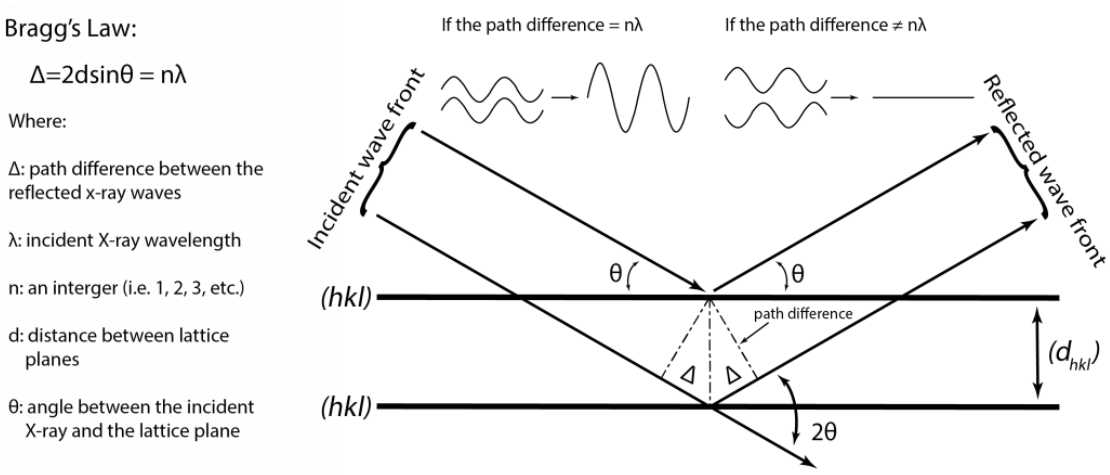

Figure 2.4 Mechanism of X-ray diffraction. (Department of Chemical & Materials Engineering, 2025)

2.5.2 Field emission scanning electron microscopy (FESEM)

FESEM is a powerful technique for examining solid samples in micrometer to nanometer scale range. It has wide applications across various disciplines, including chemistry, biology, physics and engineering (Rohde, 2011). FESEM is widely used in zeolite research because it can provide information about the morphology, structure, defects and orientation of the sample (Jaya, 2020).

During the characterization process, secondary electrons (SE) and backscattered electrons (BSE) from sample are emitted and received by detectors. The SE detector detects electrons emitted from the sample surface, which give information about surface morphology and structure. BSE detector detects BSE reflected from the sample surface, which give details about elemental composition and distribution (Zhou and Wang, 2007) (Figure. 2.5).

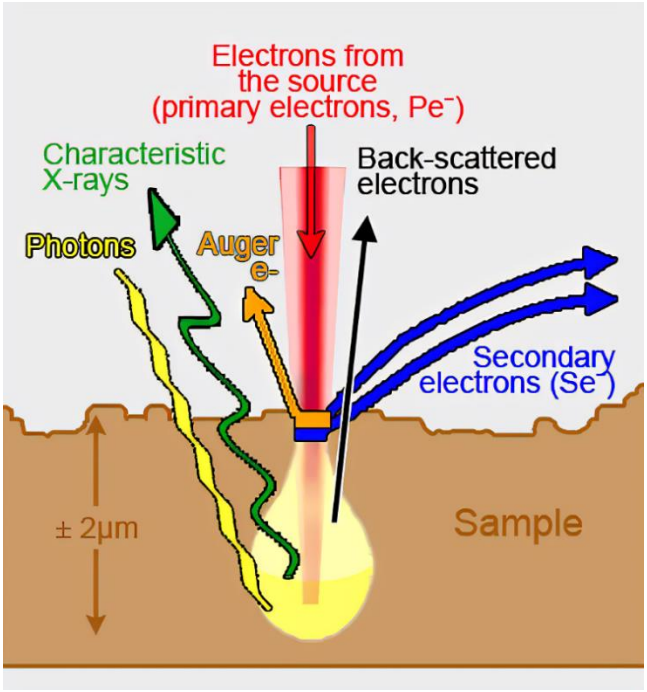

Figure 2.5 Principle of scanning electron microscopy. (Inspired Pencil, 2025)

2.5.3 Fourier transform infrared spectroscopy (FTIR)

FTIR is a spectroscopic technique that uses the interaction between infrared and molecular vibrations to obtain the information about the molecular functional groups (Hou et al., 2018). This characterization technique is simple, fast and only requires very small amount of samples for the analysis. FTIR spectroscopy can be used to analyze various types of samples, such as gases, liquids and solids. In addition, several sample preparation methods are also established, such as KBr pellet method, self-supporting wafer technique, mineral oil and diffusive reflectance IR Fourier transform (DRIFT) technique (Karge, 1998). Among these methods, the KBr technique is well known for its simplicity and only small amount of sample is needed for sample preparation.

FTIR is widely used to study the vibrational modes of zeolite frameworks. The structural vibrations of zeolites in FTIR spectra can be shown in the fingerprint region of 1300-400 cm^{-1} (Table 2.2) (Karge, 1998, Knözinger and Huber, 1998).

Table 2.2 Possible vibration bands in the fingerprint region of zeolite frameworks

Wavenumber (cm-1)	Peak assignments*
Internal tetrahedra	
1250-920	Asymmetrical streching vibrations of O-T-O
720-650	Symmetrical stretching vibrations of O-T-O
500-420	Bending vibrations of T-O
External linkages	
1050-1150	Asymmetrical streching vibrations of O-T-O
750-820	Symmetrical stretching vibrations of O-T-O
500-650	Double ring vibrations (D4R, D5R or D6R)
300-420	Pore-opening vibrations

*T = Tetrahedra Si and/or Al units.