

**CRYSTALLIZATION AND CATALYTIC
BEHAVIOR OF ORGANO-TEMPLATE FREE K-F
ZEOLITE NANOCRYSTALS IN ALDOL
CONDENSATION OF BENZALDEHYDE AND
HEPTANAL**

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UNIVERSITI SAINS MALAYSIA

2017

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HEPTANAL**

by

WONG SIEW FANG

**Thesis submitted in fulfillment of the requirements
for the degree of
Master of Science**

November 2017

ACKNOWLEDGEMENT

First and foremost, I would like to express my profound gratitude and thankfulness to my mother for supporting my decision to pursue my dreams in studying Master degree in chemistry, and for all the moral and financial support, advices and love that she gave to me during my postgraduate studies. Not to forget my family members who always gave me encouragement and spiritual support during my difficult times.

Besides, I would like to express my deepest gratitude and appreciation to my supervisor Assoc. Prof. Dr. Ng Eng Poh for his expert guidance, valuable suggestions, enthusiastic support, constant attention and immense knowledge throughout my research projects. His fruitful ideas throughout the research work had helped me in completing this project successfully apart from learning so much about the zeolite chemistry.

I would also like to thank Assoc. Prof. Dr. Jatuporn Wittayakun for his valuable advices, guidance and insight whenever I consulted him during my research attachment in Suranaree University of Technology, Nakhon Ratchasima, Thailand. My special thanks go to Krittanun Deekanwong who always took care of me during my stay in Thailand and his guidance, motivation and help throughout my research works. Additionally, I want to express my appreciation to Narongrit Sosa for his advices and guidance in performing Aldol condensation reaction. I would also like to thank the research group members in Suranaree University of Technology, Thailand under supervision of Assoc. Prof. Dr. Jatuporn Wittayakun for their help and friendship. I truly appreciate working with them.

Special thanks to the Dean of School of Chemical Sciences, Prof. Afidah Abdul Rahim for her permission to let me use all the brilliant equipments and facilities in completing my research project. I would also like to extend my sincere gratitude to all the science officers and technical staff for their various contributions directly or indirectly in analyzing all my samples throughout my study.

Last but not least, I want to thank my friends and all close members of postgraduate room of the School of Chemical Sciences especially Chow Jack Hao, Logeswary A/P Gopal, Andrew Thor Yih Yang and Tan Kok Hou for their help, support and encouragement during my study in Universiti Sains Malaysia. Our friendship will definitely stay forever inside my heart. In addition, special thanks to the financial support from FRGS (203/PKIMIA/6711495), RUI (1001/PKIMIA/8011012) and SATU Joint Research Scheme (RUI018O-2016). Lastly, I am also sincerely thankful to the Ministry of Higher Education Malaysia for the scholarship, Mybrain15 provided.

Wong Siew Fang

November 2017

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LIST OF ABBREVIATIONS, NOMENCLATURES AND SYMBOLS

°C	Degree celsius
Å	Angstrom (1×10^{-10} m)
Al	Aluminum
AlO ₄	Alumina tetraoxide
Al(OH) ₃	Aluminum hydroxide
ca.	Circa (approximately)
D6R	Double 6 rings
DMSO	Dimethyl sulfoxide
EDI	Edingtonite
F ⁻	Fluoride ion
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
HRTEM	High resolution transmission electron microscopy
h	Hour(s)
IZA-SC	International Zeolite Association Structure Commission
KBr	Potassium bromide
KOH	Potassium hydroxide
M	Molarity
mg	milligram
min	Minute(s)
MOS	Magnesium organo silicate
NaOH	Sodium hydroxide
nm	nanometer (1×10^{-9} m)

O ₂	Oxygen molecule
OH ⁻	Hydroxide ion
PBU	Primary building unit
PP	Polypropylene
PSA	Pressure swing adsorption
PTFE	Polytetrafluoroethylene
ppm	Part per million
RHA	Rice husk ash
SAED	Selected area electron diffraction
SBU	Secondary building unit
SDAs	Structure-directing agents
Si	Silicon
SiO ₂	Silicon dioxide
SiO ₄	Silicon tetraoxide
SS MAS NMR	Solid state magic angle spinning nuclear magnetic resonance
TMA	Tetramethylammonium
TPA	Tetrapropylammonium
VOCs	Volatile organic compounds
wt%	Weight percentage
XRD	X-ray diffraction
XRF	X-ray fluorescence spectroscopy

**PENGHABLURAN DAN SIFAT PEMANGKINAN NANOHABLUR ZEOLIT
K-F TANPA ACUAN ORGANIK DALAM KONDENSASI ALDOL
BENZALDEHID DAN HEPTANAL**

ABSTRAK

Tujuan projek ini adalah untuk mengkaji pertumbuhan nanohablur zeolit K-F (kod struktur EDI) yang disintesis melalui campuran reaktan tanpa acuan organik. Nanohablur zeolit K-F telah disintesis dalam keadaan hidrotermal. Zeolit K-F dengan morfologi kuboid telah diperolehi dalam masa 3.0 jam pada 100 °C. Nanohablur tersebut cenderung untuk menggumpal dan membentuk zarah sekunder berbentuk sfera. Di samping itu, nanohablur zeolit K-F juga telah disintesis di bawah sinaran gelombang mikro pada 100 °C dan abu sekam padi (RHA) telah digunakan sebagai sumber silika alternatif. Kadar penghabluran telah dipertingkatkan dengan begitu ketara dan nanohablur zeolit K-F telah diperolehi dalam masa 10 minit. Nanohablur zeolit K-F juga digunakan sebagai mangkin pepejal bes dalam tindak balas kondensasi Aldol heptanal dengan benzaldehid dengan kehadiran gelombang mikro. Nanohablur zeolit K-F menunjukkan prestasi pemangkinan yang baik dalam tindak balas yang dikaji dengan 77.1% penukaran heptanal dan 69.5% pemilihan kepada jasminaldehid pada 180 °C selama 40 minit. Mangkin nano tersebut dapat diguna semula dan tiada kehilangan yang ketara dalam kereaktifan mangkin walaupun selepas lima kitaran tindak balas berturutan.

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ABSTRACT

The aim of this project was to study the crystal growth of K-F zeolite nanocrystals (structure code EDI) synthesized from organo-template-free precursor mixture. K-F zeolite nanocrystals were synthesized under hydrothermal condition. Fully crystalline nanosized K-F zeolite crystals with flattened cuboid shape morphology were obtained within 3.0 h at 100 °C. These nanocrystals tended to agglomerate to form secondary spherical particles. K-F zeolite nanocrystals were also synthesized under microwave irradiation at 100 °C where rice husk ash (RHA) was used as an alternative silica source. The crystallization rate was significantly enhanced and fully crystalline K-F zeolite nanocrystals were obtained within 10 min. The K-F nanozeolite was used as a solid base catalyst in Aldol condensation reaction of heptanal with benzaldehyde under microwave condition. The nanosized K-F zeolite crystals showed good catalytic performance in the studied reaction with 77.1% heptanal conversion and 69.5% jasminaldehyde selectivity at 180 °C after 40 min. The nanocatalyst was reusable and no significant loss in its catalytic reactivity was observed even after five consecutive reaction cycles.

CHAPTER 1

INTRODUCTION

1.1. General introduction

Zeolites are hydrated inorganic porous aluminosilicate materials having a highly ordered crystal structure with a pore size range from 2 to 12 Å [1]. Zeolites have a chemical composition very similar to sand as they are mainly constructed by Al, Si and O elements. All zeolites have unique three-dimensional open framework structured of AlO_4 and SiO_4 tetrahedral units that are linked together by sharing oxygen atoms [2]. There are 67 types of naturally occurring zeolites which have been discovered over the past 200 years and 232 unique zeolite frameworks have been successfully identified and approved by the International Zeolite Association Structure Commission (IZA-SC) [3]. Some common natural zeolites (e.g. mordenite and chabazite) and synthetic zeolites (e.g. zeolite A, ZSM-5, X and Y) are commercially used due to their distinctive ion exchange, adsorption and catalytic properties. Currently, global zeolite market size was valued at around USD 3.50 billion in 2014 and is expected to achieve USD 4.50 billion in 2020 due to the growing demand for detergents and rising refining output [3, 4].

Traditionally, zeolites are synthesized with crystal aggregates or micron-sized crystals. Recently, the synthesis of nanocrystalline zeolites with molecular dimension (<100 nm) has received worldwide attention especially in the catalysis community [4]. This is probably due to the great interest in the crystal growth of zeolite materials and their fundamental studies on the nucleation stage of zeolites [5]. The decrease in particle size from micrometer to nanometer dimension leads to significant changes in the zeolite properties which make them as an important material for many technical

applications, particularly in zeolite membranes [5], production of ultra-thin zeolite films [6], catalysis [7], lubricants [8], drug delivery [9] and medicine [10]. Therefore, nanosized zeolites are more favorably used than conventional micrometer-sized zeolites considering their unique physicochemical properties such as small particle size, large external surface area and reduced intracrystalline diffusion path lengths [4].

Generally, zeolite nanocrystals with narrow particle size distribution are synthesized from colloidal clear aluminosilicate solution [11]. Abundant amounts of organic templates such as tetrapropylammonium cations (TPA⁺) and tetramethylammonium cations (TMA⁺) are used in order to produce super-saturation condition for crystallization of nanocrystals. Besides, these costly and harmful organic templates are usually introduced to the gel precursor as structure-directing agents (SDAs) with the aim to control the crystallite size and to direct the formation of specific crystalline framework of the zeolite materials [12]. To obtain nanocrystalline solids, the crystallization process is carried out at moderate temperature from a period of time of hours to several days. Nevertheless, these synthesis recipes are environmentally unfriendly and non-economically viable because of long crystallization time, low crystalline yield (<10%) and high consumption of very high-priced organic templates [13, 14]. After the synthesis, the organic templates need to be removed *via* high temperature calcination [15] in order to open up the porosity. This practice make the synthesis of nanozeolites industrially unfavorable. To address this issue, many synthetic strategies such as ionothermal [16], seed-induced [17] and confined space [18] approaches have been used to replace the typical templating approach.

Besides that, in the typical zeolite synthesis, most of the silica sources used are commercially available in the gel form, fumed solid or colloidal silica solution [19].

Over the past 20 years, extensive studies have been performed on the synthesis of zeolites from agricultural wastes such as rice husk [20], corn cobs [20] and sugarcane bagasse [21]. Nanocrystalline zeolites can be synthesized from organic template-free system using these agricultural wastes such as rice husk ash (RHA). RHA has been widely used in the synthesis of nanostructured materials due to its high silica content (up to 98% SiO₂) [22]. Compared to other conventional silica source (e.g. harmful and high-priced tetraethylorthosilicate, fumed silica or water glass), RHA is considered as a cheap, highly active and an eco-friendly silica source. Therefore, the optimization and development of high quality amorphous agro-silica source will have immense impact on the synthesis of nanoporous materials [23].

The study on the synthesis of classical micron-sized zeolites have been widely studied. However, there are limited papers reporting on the microscopic investigation of the nucleation, crystallization and catalytic behavior of nanosized zeolites particularly potassium-based zeolites. Therefore, a comprehensive study on the investigation of the chemical process occur during nucleation and crystallization stages in these potassium-rich zeolite nanocrystals is worth to be further explored. In addition, this study is also dedicated on the synthesis of nanosized potassium-rich zeolites free of organic SDAs (or template) for achieving the goal of green chemistry. The synthesized zeolites are then used as basic catalysts for the synthesis of jasminaldehyde.

1.2. Research objectives

This research is performed based on the following specific objectives:

- a) To study the growth of K-F zeolite nanocrystals in organotemplate-free system under hydrothermal condition.

- b) To investigate the formation of nanosized K-F zeolite from rice husk silica *via* microwave irradiation.
- c) To study the catalytic behavior of K-F nanozeolite in Aldol condensation reaction of heptanal and benzaldehyde under microwave condition.

1.3. Overview of the thesis

This thesis is divided into five chapters, which clearly explain the background, experimental procedures and research findings of the project. Chapter 1 is an introduction explaining the nanocrystalline zeolites and the potential use of RHA in the zeolite syntheses. Chapter 2 is a comprehensive literature review elaborating the history of zeolites, zeolite framework structures and properties, the use of agro-silica in zeolite synthesis, fundamental concepts of zeolite formation and the applications of zeolites in multiple areas.

Chapter 3 presents the synthesis of K-F (EDI-type) zeolite nanocrystals in organic-template-free system under hydrothermal condition. Besides, the crystal growth study of K-F nanozeolites by various microscopic and spectroscopic techniques is reported in this chapter. Chapter 4 reports the synthesis of K-F zeolite nanocrystals from rice husk silica using microwave heating. Prior to zeolite synthesis, the silica ash is extracted from rice husk using nitric acid treatment followed by combustion at 600 °C for 12 h. Then, the rice husk ash is used as a silica source together with other chemical reagents in synthesizing the zeolite nanocrystals. The synthesis is carried out in PTFE reaction vessels under microwave irradiation. The solid sample is purified and analyzed by microscopy and spectroscopy characterization techniques. The porosity and the basicity of K-F nanozeolite are also evaluated by nitrogen sorption analysis and temperature-programmed desorption of carbon dioxide

(CO₂-TPD), respectively. The nanosized K-F zeolites are then applied as a solid base catalyst in Aldol condensation reaction between benzaldehyde and heptanal under microwave irradiation. The reaction products are analyzed and identified using a gas chromatography with flame ionization detector (GC-FID) and a gas chromatography coupled with mass spectrometry (GC-MS), respectively. Moreover, the zeolite catalyst recyclability is also tested.

Chapter 5 concludes the work based on the research findings obtained. In addition, suggestions for the future work of this research are also given to broaden the prospect of using the RHA agro-waste as an alternative silica source for the synthesis of other micro- and mesoporous materials whereas nanosized zeolite itself can also be applied in many potential applications.

CHAPTER 2

LITERATURE REVIEW

2.1. Zeolites

Zeolites are hydrated porous crystalline materials with unique framework structures constructed of corner-sharing alumina (AlO₄) and silica (SiO₄) tetrahedra units [24]. Each AlO₄ tetrahedron in the framework structure is negatively charged which can be counter-balanced by the extra-framework cations (mainly alkali and alkali-earth metal ions). Thus, it creates a strong electrostatic field on the zeolite's surface (Figure 2.1).

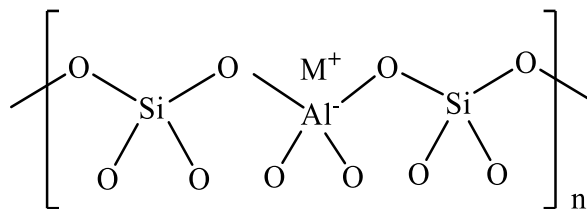
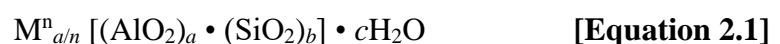


Figure 2.1. The basic structure of zeolites, where the negative charge of Al sites is counter-balanced by positively charged metal cations (M⁺).

The zeolite framework structures contain cages or interconnected voids of discrete size which are usually occupied by water molecules and the charge balancing extra-framework cations [25]. These cations are mobile and usually undergo ion exchange. On the other hand, the water molecules can be removed reversibly *via* heat application [26].

Chemically, the empirical formula of zeolites can be represented by Equation 2.1 [27]:



where M is the exchangeable cations of valence n . M^n may either be an alkali (Group 1) or alkaline earth (Group 2) metal cations. These positive ions may either be added *via* ion exchange post-synthesis treatment or during the synthesis. The values of a and b are the total numbers of tetrahedra per unit cell ranging from 2 to 200 and c indicates the number of water molecules contained in the interconnected voids of the zeolites. The structural formula of a zeolite is defined according to the crystallographic unit cell [26].

In addition, zeolites have regular structures and pore sizes that give them a spongy-like appearance (Figure 2.2) [28]. Basically, pore shape, pore diameter and the way these pores are interconnected can be used to differentiate the type of zeolites [28]. Moreover, the pore size plays a vital role in the use of zeolites. For instance, large pore zeolites are normally used in catalysis whereas small pore zeolites are used in gas separation.

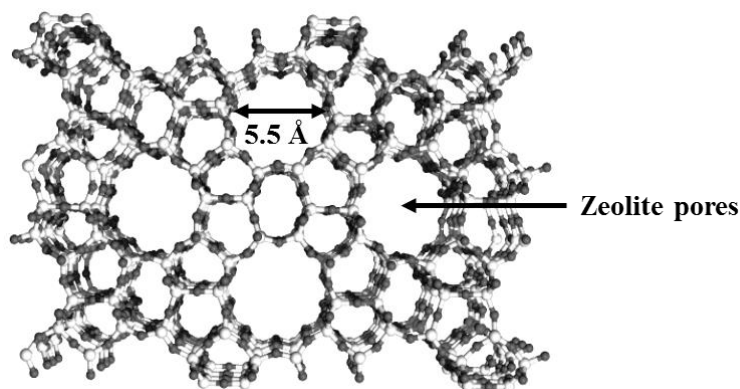


Figure 2.2. Zeolite structure with its pores [29].

2.2. Discovery and history of zeolites

The zeolite history started in 1756 when Alex Fredrick Crönstedt, a Swedish mineralogist, discovered the first natural occurring mineral, stilbite [30]. He found that upon quickly heating the mineral stilbite in a blowpipe flame, it released huge amount of occluded water that had been adsorbed by the mineral [31]. Hence, he named the new mineral a “zeolite” which derived from two classical Greek words, *zeo* and *lithos*, with the meaning of boiling stone, because of the ability to evaporate water when heated to about 200 °C [31]. He then categorized zeolites as a new class of minerals which composed of hydrated aluminosilicates of the alkali and alkaline earths.

In 1857, the hydration-dehydration properties of zeolites were demonstrated by Damour [32]. Weigel and Steinhof managed to separate the gas molecules on the basis of size upon the removal of water molecules from the zeolite internal structure in 1925. The zeolite mineral was then identified for the first time by Leonard using X-ray diffraction in 1927 [33]. In 1930, the first single crystal structures of zeolite minerals were described by Taylor and Pauling [34, 35]. Chabazite and Mordenite were successfully synthesized by Barrer in 1938, leading to the potential applications in industrial air purification and separation [36]. Further discovery of commercially significant zeolites types A, X and Y was done by Milton and his coworker, Donald W. Breck between 1949 and 1959. In 1954, zeolites were used as selective adsorbents and catalysts for industrial purifications and separations. Nowadays, zeolites are used in many applications due to their unique porous properties.

Basically, when volcanic rocks and ash layers react with alkaline groundwater, it creates natural zeolites. Besides, zeolites also crystallize in shallow marine environments for a period of thousands to millions years. Over the past 200 years, 67 types of natural zeolites such as chabazite, analcime, heulandite, leucite and pollucite

have been discovered [37]. Naturally occurring zeolites are usually easy to exploit and use after simple treatments, hence have a lower cost associated with it [38]. However, natural zeolites are rarely pure due to the contamination with other metals or minerals. Because of this, natural zeolites become less favorable in many important commercial applications where the purity is essential. In recent years, more than 200 zeolites have been synthesized in the laboratory. Synthetic zeolites have numerous advantages such as better ion exchange ability, high purity and uniform pore size distribution when compared to natural zeolites [39]. For example, synthesized zeolites type X, Y, A and ZSM-5 have many potential industrial applications due to their distinct ion-exchange, adsorption and catalytic properties.

2.3. Zeolite structures and properties

Zeolite structures are essentially composed of primary and secondary building units. Compared to secondary building unit (SBU), a primary building unit (PBU) is the simpler building block. This is because, the PBU of the zeolite structure has a central ion of either aluminum cation (Al^{3+}) or silicon cation (Si^{4+}) which are surrounded by four oxygen anions (O^{2-}) in TO_4 tetrahedra units (Figure 2.3a) [38]. A macromolecular tridimensional tetrahedron is formed when two tetrahedra are joined together by sharing an oxygen atom (Figure 2.1). Other simple polyhedra structures such as cubes, pentagons, hexagonal prisms or cubo-octahedra called secondary building units (SBUs) can be created by the combination of PBUs [40]. The final framework structures are made up of assembly of the SBUs.

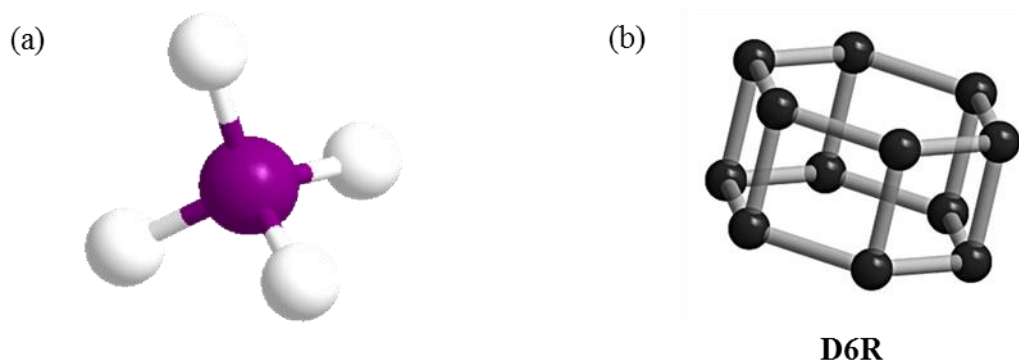


Figure 2.3. (a) The primary building unit (PBU) and (b) secondary building unit (SBU) of zeolite structure in TO_4 ($T = \text{Al}$ or Si) tetrahedron [40, 41].

The secondary building units (SBUs) usually are composed of m -ring structures, in which m is referred to 4, 6, 8, 10 or 12 (Figure 2.3b) [41]. In addition, cages and channels which are essential elements of all zeolite structures can be formed by the linkage of secondary building units. Zeolite structures are typically complex due to the different ways in tetrahedral group that are connected by the same sharing oxygen atom to form polynuclear complexes. Because of this reason, zeolites and zeolite-like materials with different diversity can be formed.

Besides, zeolite structures can also be explained on the basis of the geometry, size and the connectivity of the pore space [38]. The zeolite structures have a uniform pore system with one, two or three dimensional channels and additional inner cavities. Different types of zeolites are different in channel dimensions. The channels may be tubular shape, zig-zag or circular [42]. The pore diameter channels range from 3 Å to 10 Å (0.3 to 1.0 nm) which are quite similar to the dimension of many hydrocarbon molecules when they are applied in adsorption and catalysis. In addition, the pore volumes of zeolites are from about 0.10 to 0.35 cm^3/g [27]. However, the exact pore diameter depends on the coordination and the number of cations and anions existed in the ring [43]. Table 2.1 shows the classification of zeolites according to the pore size.

Table 2.1. Classification of zeolites according to the pore size [44].

Types of zeolite	Pore diameter	Zeolites (Structure type)
Small pore zeolites (8-membered ring pores)	0.30 to 0.45 nm	Chabazite (CHA) Edingtonite (EDI) Zeolite P (GIS) Zeolite A (LTA)
Medium pore zeolites (10-membered ring pores)	0.45 to 0.60 nm	Ferrierite (FER) ZSM-5 (MFI) ZSM-11 (MEL) Stilbite (STI)
Large pore zeolites (12-membered ring pores)	0.60 to 0.80 nm	Cancrinite (CAN) Mordenite (MOR) Zeolite X (FAU) Zeolite Y (FAU)
Extra-large pore zeolites (14-membered ring pores)	> 0.80 nm	CIT-5 (CFI) ITQ-33 (ITT) OSB-1 (OSO) UTD-1F (DON)

2.4. Linde type F (EDI)

Zeolite K-F is a potassium-type zeolite. It is a member in the Edingtonite family. Zeolite K-F was synthesized for the first time by Barrer and his coworker, Baynham in 1956 [45]. Zeolite K-F has a EDI-type framework structure and is made up of several natrolite units joined together by oxygen bridges to form natrolite chains (or fibrous chains) [46] where the natrolite unit consists of four four-membered rings (4MR). A natrolite unit is shown in Figure 2.4.



Figure 2.4. A natrolite secondary building unit [46].

The EDI-type framework composed of cross-linked chains of T_5O_{10} tetrahedra characterized by the apertures of two different types of 8-membered ring channel systems with a diameter of $2.8 \times 3.8 \text{ \AA}^2$ and $2.0 \times 3.1 \text{ \AA}^2$ (Figure 2.5) [47]. Thus, it possesses a three-dimensional pore channel structure with pores running perpendicular to each other in the x, y and z planes (Figure 2.6). These channel systems are interconnected by oxygen bridges and the potassium cations (K^+) are located inside them with water molecules as guest molecules [48].

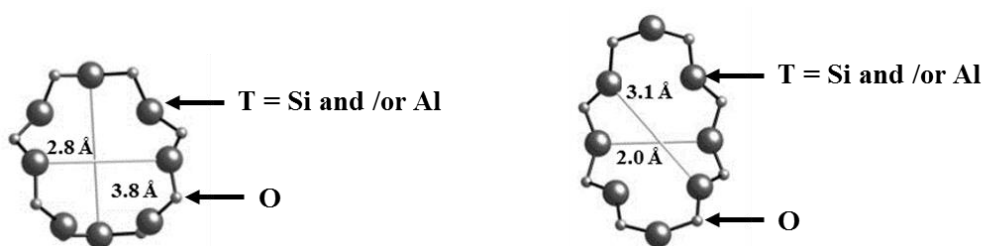


Figure 2.5. 8-membered ring channel systems of EDI-type framework structure [46].

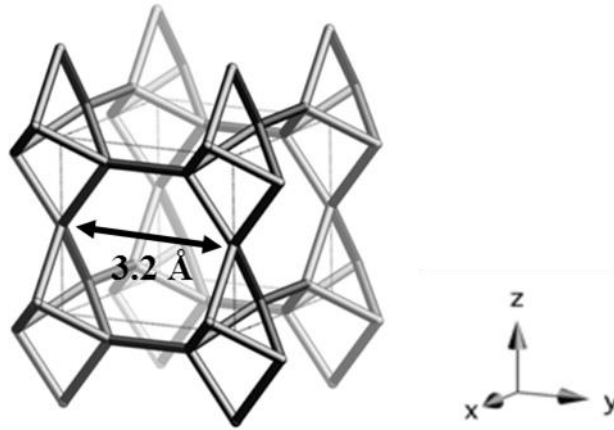


Figure 2.6. Framework structure of EDI-type zeolite (zeolite K-F) viewed along the [110] direction [46].

Zeolite K-F is a small-pore zeolite as the pore diameter of the channels is about 3.2 \AA (0.32 nm) [49]. Zeolite K-F has a void volume fraction of 0.67 and the Si/Al ratio of this zeolite is generally between 1 and 2 [50]. Zeolite K-F has a very high temperature stability (usually up to above $1050 \text{ }^\circ\text{C}$) [51]. The empirical formula of zeolite K-F can be expressed by $\text{KAlSiO}_4 \cdot 1.5\text{H}_2\text{O}$, which approaches an ordered arrangement of Si and Al atoms in the zeolite framework [52].

Typical synthesis of zeolite K-F involves hydrothermal crystallization of aluminosilicate gels or by re-crystallization of other aluminosilicates under alkaline media [53]. Besides, various alumina sources (e.g. acidic alumina solution, aluminum hydroxide hydrate, aluminum isopropoxide and aluminum foil) and silica sources (e.g. acidic silica solution, fumed silica, colloidal silica and silica gel) have been used to synthesize zeolite K-F [53-55]. Presently, low-cost raw materials, including volcanic rocks [47], natural kaolin [48], coal fly ashes [49], clay ores [52], kaolinite [56], and paper sludge ashes [57], that contain Al and/or Si sources are also used to synthesize zeolite K-F.

Occasionally, organic additives such as tetraethylammonium cation (TEA⁺) and metal amine complexes are used as structure directing agents (SDAs) for the synthesis of EDI-type zeolite [55]. However, the organic template that is used in the synthesis has several drawbacks such as harmful, non-recyclable, environmentally unfriendly and costly [58]. A summary of the literature procedures for Linde type F zeolite synthesis is reported in Table 2.2.

Table 2.2. A comparison of Linde type F zeolite synthesis conditions.

Compositions	Methods	Conditions	Ref.
3.3SiO ₂ :1Al ₂ O ₃ :1K ₂ O:3H ₂ O	Reflux	95 °C, 48 h	[49]
2SiO ₂ :1Al ₂ O ₃ :5Li ₂ O:275H ₂ O	Hydrothermal	90 °C, 16 h	[50]
2.01SiO ₂ :1Al ₂ O ₃ :1.32K ₂ O:3.34H ₂ O	Hydrothermal	90 °C, 10 days	[51]
2SiO ₂ :1Al ₂ O ₃ :1K ₂ O:3H ₂ O	Hydrothermal	80 °C, 12 days	[53]
1SiO ₂ :0.5Al ₂ O ₃ :3Li ₂ O:410H ₂ O	Microwave heating	90 °C, 60 min	[54]
4.16SiO ₂ :1Al ₂ O ₃ :0.05Na ₂ O:244H ₂ O: 2.37(TMA) ₂ O: 0.5CuO:15NH ₃	Hydrothermal	100 °C, 3 days	[55]
2SiO ₂ :1Al ₂ O ₃ :3K ₂ O:88.3H ₂ O	Hydrothermal	100 °C, 27 h	[58]
2SiO ₂ :1Al ₂ O ₃ :1K ₂ O:86.3H ₂ O	Hydrothermal	175 °C, 24 h	[59]

Zeolite K-F can be used in industrial applications. For instance, zeolite K-F has been applied in waste-water cleaning and purification processes due to its high selectivity for the uptake of ammonium cations (NH₄⁺) [60]. Apart from that, zeolite K-F is also significantly useful for soil amendment because of its high affinity towards ammonium cations (NH₄⁺) [61].

2.5. Amorphous silica source from agricultural wastes

Paddy rice covers about 1% of the earth's surface and grows on every mainland except for Antarctica [62]. Rice husk is an agricultural residue abundantly available in rice-milling industries with no commercial value due to its hardness and low nutritive value [63]. The major compositions of rice husk are silica, cellulose and lignin depending on the climate and geographical growth location. Rice husk is one of the most silica-rich raw materials which contains 87-98% silica in an amorphous form together with trace amounts of metallic impurities after complete combustion [63]. Because of high silica content in the rice husk, it becomes economical to extract silica from the ash and then use it as raw material to synthesize various types of inorganic crystalline porous compounds [64]. Acid leaching treatment of rice husks followed by thermal treatment at high temperature ranging from 550 to 700 °C for a period of time has been proven as an efficient way to remove most of the metallic impurities and hydrocarbons in order to produce white silica ash with high silica content and high surface area [65]. For instance, the silica yield can be enhanced from 72.1 to 98.0 wt% by calcination of acidified rice husk at 700 °C for 6 h [65]. Recent studies revealed that the optimum temperature for producing amorphous silica is about 600 to 700 °C in order to avoid any transformation of amorphous phase to unwanted crystalline dense phase [66].

2.6. Zeolite synthesis and formation

Basically, various methodologies can be used to synthesize zeolites with different structures, properties and compositions. Zeolites can be formed naturally from volcanic ash while synthetic zeolites are mainly synthesized in the laboratory using standard chemical reagents. The most traditional method of zeolite synthesis is

the hydrothermal crystallization process under mild conditions (100 °C and ambient pressure) [40]. Besides, it involves a reactive aluminosilicate gel precursor composed of water, alumina (Al_2O_3) and silica (SiO_2) sources in the presence of alkali hydroxides (e.g. NaOH, KOH or CsOH) under high pH (basic) environment [36]. The complex chemical processes involved in this transformation can be known as zeolitization. In general, alumina sources can be found in the form of hydroxide, salts, isopropoxide, or aluminate. Whereas, silica sources such as silica sol, sodium silicate, amorphous silica, or fumed silica are commonly used. Zeolites can have different physico-chemical properties depending on the aluminum content in the framework. In certain cases, the addition of organic quaternary ammonium cations as a template or structure-directing agent (SDA) to the alkaline gel is needed in order to stabilize the formation of desired zeolite framework structure [40].

The chemical stoichiometry of the final zeolitic crystalline products can be resembled by the synthesis gel composition. Basically, zeolite synthesis process can be described by three steps which are induction, nucleation and crystallization. The synthesis begins with the formation of a hydrous aluminosilicate amorphous gel phase by mixing aluminate and silicate solutions together with a cation source under a high pH medium, in which the source of aluminum and silicon is either monomeric or polymeric form [67]. In some cases, this initial amorphous gel is aged at an intermediate temperature for a period of time in order to allow initial nucleation of the gel system. Then, the aqueous synthesis mixture is placed in a closed hydrothermal system at increasing temperature either in a polypropylene (PP) bottle (for synthesis ≤ 100 °C) or a Teflon-lined stainless steel autoclave (for synthesis ≤ 250 °C) for a varying time (few hours to several days) until the desired level of product crystallinity is achieved [68].

In general, the type of the zeolites produced can be determined by many factors, including the crystallization temperature and time, the organic template molecules used, the chemical nature of the reactants (alumina and silica sources), the pH of the system, the composition of the synthesis mixture (silica to alumina ratio, inorganic cations, mineralizing agents) and the sequence of mixing the reactants [69-70]. These synthesis parameters have significant influences on the zeolite formation. For instance, silica/alumina ($\text{SiO}_2/\text{Al}_2\text{O}_3$) ratio in the reaction system plays an important role in determining the structure and composition of the synthesized zeolite crystals [36]. Besides, the use of organic templates are aimed to control the crystallite size and to direct the formation of specific zeolite framework structures [12]. Moreover, variation of water content not only reduce the crystallinity and crystal size of zeolites, but also change the crystallization region of zeolite phases [40]. Furthermore, the crystallinity and crystal size of zeolite materials also significantly influenced by the crystallization time and temperature [70]. The important role of chemical sources in the zeolite synthesis are reported in Table 2.3.

Table 2.3. Chemical reactants and their roles in zeolite synthesis [32].

Chemical sources	Functions
Alumina (Al_2O_3)	Origin of the framework charge
Silica (SiO_2)	Primary building units (PBU) of the framework
Water (H_2O)	Solvent, guest molecule
OH^- , F^-	Mineralizer, guest molecule
Alkali cations	Counter ions of the framework charge, guest molecules
Organic structure directing agent	Counter ion of the framework charge, template agent

The amorphous gel starts to dissolve in the reaction solution and an intermediate in an oligomeric aluminosilicate form is formed depending on the synthesis conditions. After the amorphous gel raises to the reaction temperature, the precursors sometimes remain amorphous and no crystalline phases are detected where this period is known as the induction time. The induction period ends when the very first crystals are started to form. The desired crystalline phases can be detected after the induction period. This stage is called as the crystallization period where all the amorphous materials are gradually transformed into the final crystalline zeolite products [71]. The resulting zeolite products are then recovered from the mother liquor upon the completion of crystallization process *via* filtration or centrifugation, followed by washing and purifying until it reaches pH of 7, and drying prior to any potential applications. Calcination process will be performed at high temperature (550 °C) with the aim to remove the templates if any organic templates are used in the synthesis. All the steps involved in the hydrothermal zeolite synthesis are illustrated in Figure 2.7.

The zeolite synthesis must be reproducible and the synthesized zeolite particles must possess the same features each time it is synthesized in order to make the synthesis process industrially feasible. This aims to create the exact product optimization conditions [36].

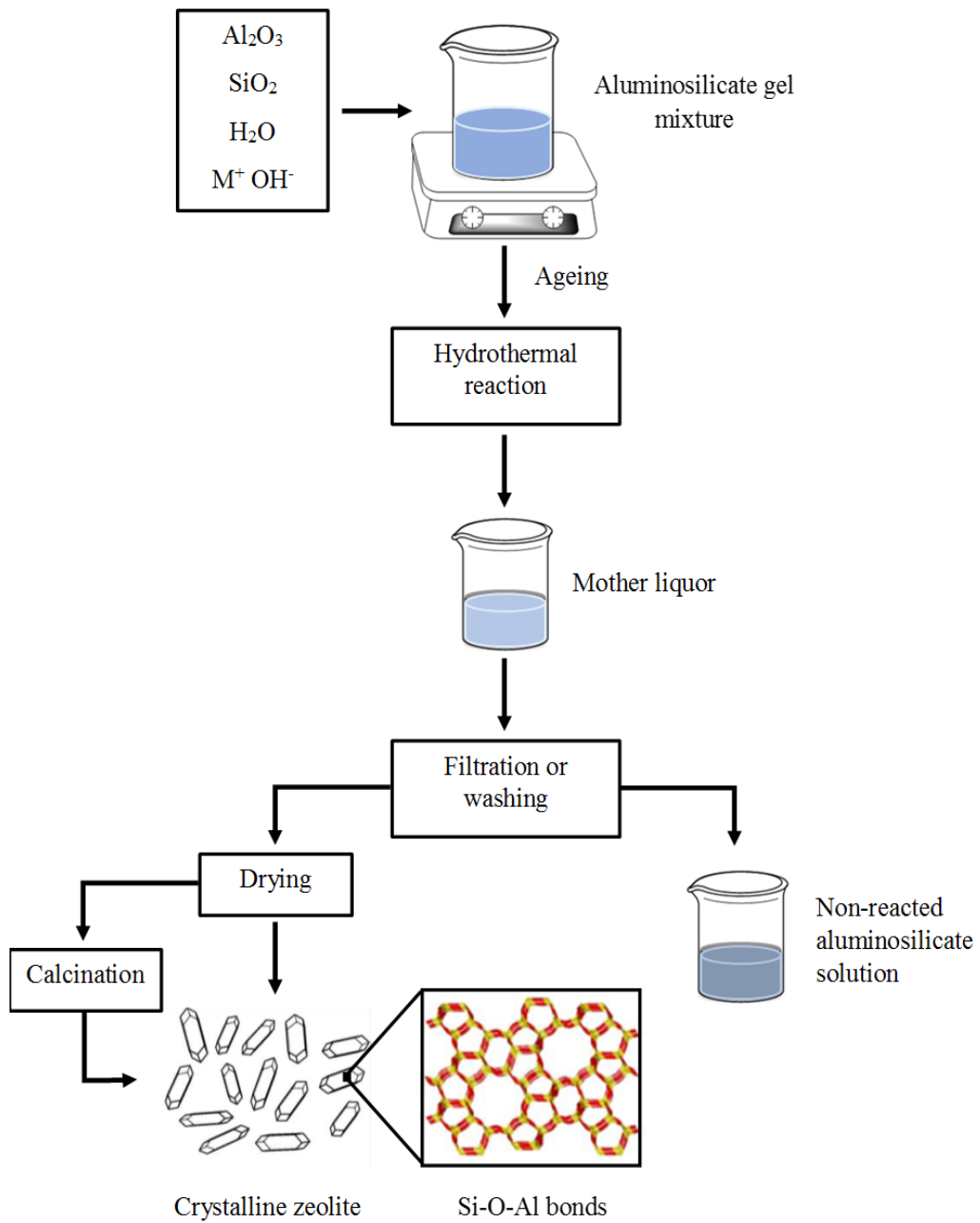


Figure 2.7. Illustration of hydrothermal zeolite synthesis process [72].

2.7. Applications of zeolites

Zeolites have a widespread of potential applications. Presently, the use of zeolites is promising and applicable in nearly all fields of human life especially in industrial sections. They can be used for gas purification and separation, petrochemical cracking, ion-exchange purposes (purification and water softening), agriculture, catalysis, and construction [73]. Moreover, natural zeolites are used in bulk mineral applications due to their low cost property. Primarily, zeolites are extensively applicable to these three applications which are adsorption, ion-exchange and catalysis.

2.7.1 Zeolites in adsorption and separation

Zeolites can be used in gas adsorption due to their shape selectivity properties. The ability to essentially adsorb particular molecules while rejecting others has lead to selective adsorption by the zeolites [73]. This is simply due to the size and shape of the pores that control the diffusion of molecules into the zeolites.

Besides, zeolites can act as molecular sieves due to their regular channel network that provide magnificent techniques to separate molecules according to shape, size and polarity. Zeolites are primarily used to purify or deodorize natural gases *via* the removal of impurities such as water, carbon dioxide and sulfur dioxide [74]. In addition, cation-containing zeolites are normally used as desiccants because of their high affinity for water and are capable of adsorbing moisture from air without damaging their crystal structure. Furthermore, zeolites can be used in air separation to generate nitrogen, hydrogen and oxygen using pressure swing adsorption (PSA) columns [75].

In environmental concern, the removal of toxic ions from industrial and public wastewater have been carried out based on this occurrence. Likewise, zeolites can be

used to remove the heavy metal ions due to their comparatively high efficiency as an adsorbent [76].

2.7.2 Zeolites in ion exchange

Zeolite structures can be described as solid electrolytes. The charge-balancing cations that are integrated into the zeolites' voids can be easily exchanged with other cations as they are not part of the zeolite framework structure [73]. The enclosed channels of zeolites consist of both water molecules and the metal cations. The exchangeable metal cations are loosely bounded to the framework structure and can be readily exchanged when the zeolites are in contact with the strong solutions of other cations, and thus involve in ion exchange [77]. Besides, the water molecules can be reversibly removed from the zeolites. The properties of zeolite products used in catalysis and adsorption applications can be modified by cation exchange of zeolites. Particularly, zeolites can act as a water softener (e.g. uptake magnesium and calcium ions from water and release sodium ions) in detergent industry [78]. Zeolites such as clinoptilolite, zeolites type A and X are commonly used in the detergent industries [79]. Moreover, Cs^+ and Sr^{2+} radioisotopes can be readily removed by natural zeolites *via* ion exchange from radioactive waste streams [79].

2.7.3 Zeolites in catalysis

Catalyst is defined as a material that accelerates the chemical reaction rate by offering an alternate pathway (faster reaction rate) with lower activation energy. In general, the catalyst itself do not undergo any permanent chemical change at the end of the reaction [80]. Besides, only a small amount of catalyst is required to increase the reaction rate between large amounts of chemical reactants and able to generate

massive amount of products. Catalysts can be categorized into homogeneous and heterogeneous catalysts. Homogeneous catalyst is a catalyst which has the same phase as the reactants (e.g. sulfuric acid and aluminum chloride) while heterogeneous catalyst is often referred to the catalyst that exists in different phase from the reactants (e.g. titanium dioxide, zeolites and transition metals).

Zeolites can be an interesting heterogeneous catalyst in many potential applications due to their stable crystalline framework structure, good thermal stability, fixed pore diameter (< 2 nm), high internal surface area (> 600 m²/g) and non-corrosive nature [81]. However, the catalytic properties of zeolites usually depend on their physico-chemical properties. Specific catalytic properties of zeolites can be promoted by creating acidity or basicity on the surface of the zeolites *via* ion-exchange with certain cations. For example, ion exchange with ammonium nitrate or ammonium chloride solutions followed by calcination can create Brønsted and Lewis acid sites. Whereas, basic sites are produced by ion exchanging with alkali cations salts (e.g. Li⁺, Na⁺, K⁺, Cs⁺ or Ca²⁺) [82].

In addition, zeolites are extremely useful as catalysts in fluid catalytic cracking (FCC), oil refining and basic petrochemical processes. Moreover, zeolites can act as oxidation catalysts where the reactions occur in the pores and thus enable highly product control [83].

2.7.3(a). Aldol condensation of benzaldehyde with heptanal

Jasminaldehyde or α -pentylcinnamaldehyde is a famous fragrance with a floral scent. It is also an important perfumery chemical which is synthesized by the Aldol condensation of benzaldehyde and heptanal (Figure 2.8) [84]. This Aldol condensation is catalyzed by both acids and bases.

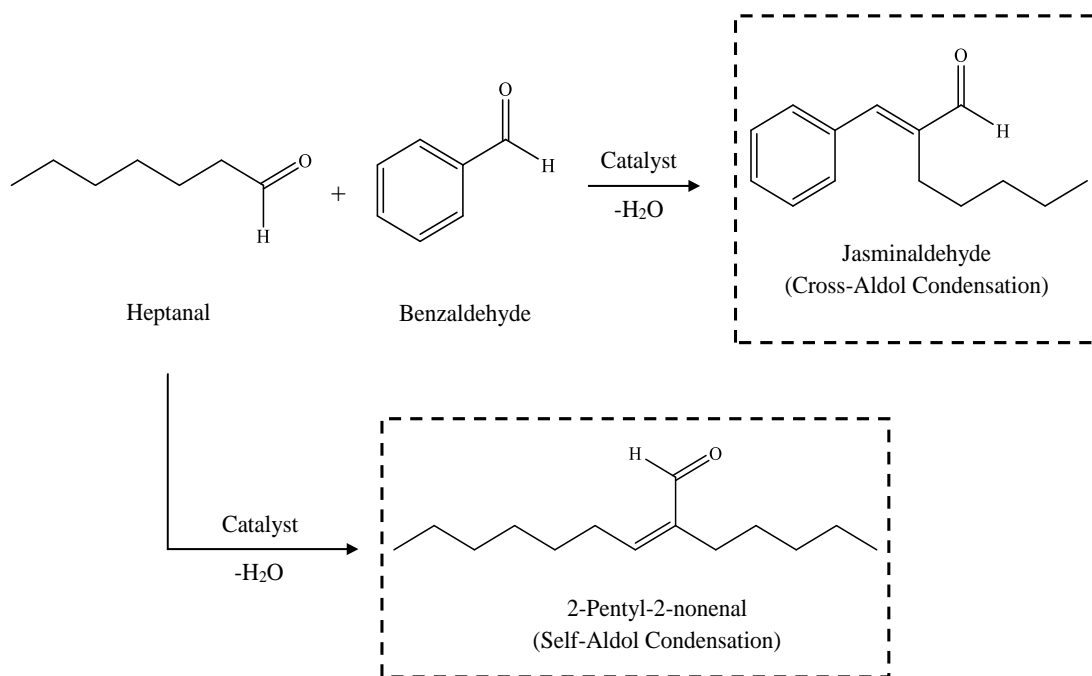


Figure 2.8. Synthesis pathway of jasminaldehyde.

Besides, this Aldol condensation reaction is a vital intermediate reaction as it produces products which can be used for the syntheses of pharmaceutical intermediates and fine chemicals. Jasminaldehyde is also extensively used in the perfume industries and the synthesis is also an interesting test reaction to assess the selectivity of the catalysts. Traditionally, this Aldol condensation is catalyzed using basic homogeneous catalysts which are mostly inorganic hydroxides such as liquid sodium or potassium hydroxide in more than stoichiometric amounts [85]. However,

there are many disadvantages of homogeneous process for the synthesis of jasminaldehyde such as lack of catalyst reusability, separation difficulty, unwanted liquid waste production, difficult reagent handling, caustic nature of liquid base like KOH, NaOH and post reaction work-up of spent liquid bases [86].

From this point of view, it is essential to use heterogeneous basic catalysts as it plays a crucial role in lowering safety risks and the amount of industrial waste. These difficulties and disadvantages can also be overcome by using solid base catalysts with good efficiency and thus providing a synthesis process having easy catalysts handling, easy products separation, high catalysts reusability and high selective towards jasminaldehyde [85]. Presently, several literatures have reported the application of various solid acid and base catalysts for the synthesis of jasminaldehyde, including beta zeolite, mesoporous Al-MCM-41, alkali exchanged zeolites, anionic exchanged resins and hydrotalcites [84-86]. However, the synthesis reactions involving the use of heterogeneous acid catalysts in the synthesis of jasminaldehyde are generally inadequate due to the lower selectivity of the products [86].

The catalytic reaction performance catalyzed by various solid acid and base catalysts under reflux condition is summarized in Table 2.4. Basically, heterogeneous acid catalysts show lower jasminaldehyde selectivity whereas heterogeneous basic catalysts give higher heptanal conversion with better jasminaldehyde selectivity.