BAMBOO LEAF ASH AS A GREEN AND SUSTAINABLE SOURCE OF AMORPHOUS SILICA FOR THE SYNTHESIS OF ZEOLITE CATALYST MATERIALS FOR CYANOETHYLATION OF ALCOHOLS

CHOW JACK HAO

UNIVERSITI SAINS MALAYSIA

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CHOW JACK HAO

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Al	Aluminum
Å	Angstrom (= 10^{-10} meters)
AlO_4	Alumina tetraoxide
BET	Brunauer-Emmet-Teller
BLA	Bamboo leaf ash
ca.	Approximately
Ca^{2+}	Calcium cation
Cs^+	Cesium cation
DTG	Derivative thermogravimetry
FAU	Faujasite
FESEM	Field emission scanning electron microscopy
FT-IR	Fourier transform infrared
h	Hour
HO^-	Alkoxy radical
HNO_3	Nitric acid
IUPAC	International Union of Pure and Applied Chemistry
IZA	International Zeolite Association
K^+	Potassium cation
KBr	Potassium bromide
Li^+	Lithium cation
LiCl	Lithium chloride
LTA	Linde-type A

M	Molarity
MR	Membered ring
N_2	Nitrogen
Na^+	Sodium cation
$NaAlO_2$	Sodium aluminate
NaOH	Sodium hydroxide
nm	naonometer
P/P_0	Relative pressure
RHA	Rice husk ash
S_{BET}	Specific BET surface area
SiO_4	Silicon tetraoxide
Si–O–Si	Siloxane
T	Temperature
t	Time
TG	Thermogravimetry
wt%	Weight percentage
XRD	X-ray diffraction
XRF	X-ray fluorescence

ABU DAUN BULUH SEBAGAI SUMBER SILIKA AMURFUS YANG HIJAU DAN LESTARI BAGI SINTESIS MANGKIN ZEOLIT UNTUK SIANOETILASI ALKOHOL

ABSTRAK

Tujuan projek ini adalah untuk mengkaji potensi penggunaan abu daun buluh (BLA) untuk sintesis jenis -LTA dan -X zeolit yang merupakan pemangkin reaksi sianoetilasi alkohol. Amurfus BLA mempunyai kandungan silika yang tinggi (99.37% SiO_2) adalah utamanya disediakan melalui rawatan asid sebelum pembakaran pada 600 °C. LTA-jenis zeolit (NaA) telah disintesis daripada BLA dalam keadaan hidroterma. Kesan sintesis (suhu pemanasan, masa dan komposisi kimia) telah dikaji kerana ia mempunyai kesan yang penting dalam pembentukan saiz purata, saiz taburan, morfologi dan ketulenan produk yang kukuh. Zeolit NaA telah digunakan lagi sebagai pemangkin untuk reaksi sianoetilasi dalam tekanan autogenus. Di samping itu, sifat kebolehgunaan semula pemangkin zeolit NaA juga telah diuji. X-jenis zeolit (topologi FAU) dengan kation logam alkali yang berbeza (Li^+, K^+, Cs^+ dan Ca^{2+}) telah disediakan melalui pertukaran ion yang mana BLA telah digunakan sebagai sumber silika. Zeolit dengan kation logam alkali yang berbeza mempunyai kekuatan bes yang berbeza. Seperti yang dijangka, CsX zeolit dengan kebesan yang terkuat menunjukkan prestasi pemangkin terbaik dalam sianoetilasi alkohol. Keputusan menunjukkan bahawa kebesan permukaan rangka kerja X zeolite beransur-ansur meningkat dalam perintah LiX < NaX < CaX <KX < CsX. Antara pemangkin disediakan, CsX dengan ciri-ciri yang paling asas memberikan prestasi pemangkin yang terbaik (97.0% penukaran) dalam kajian reaksi sianoetilasi (9 h, 150 °C, tekanan autogenus) manakala CaX sensitif kelembapan (28.2%) menunjukkan prestasi yang paling rendah di bawah keadaan yang sama.

BAMBOO LEAF ASH AS GREEN AND SUSTAINABLE SOURCE OF AMORPHOUS SILICA FOR THE SYNTHESIS OF ZEOLITE CATALYST MATERIALS FOR CYANOETHYLATION OF ALCOHOLS

ABSTRACT

The aim of this project was to study the potential use of bamboo leaf ash (BLA) for the synthesis of LTA- and X-type zeolites which were the catalysts for the cyanoethylation of alcohols reaction. The amorphous BLA with high silica content (99.37% SiO_2) was first prepared *via* acid treatment prior to combustion at 600 °C. LTA-type zeolite (NaA) was synthesized from BLA under hydrothermal condition. The effect of synthesis (heating temperature, time and chemical composition) were studied as they had significant effects on the average size, size distribution, morphology and purity of the solid products. In addition, the catalyst reusability of zeolite NaA was also tested. Zeolite NaA is found to be reactive in cyanoethylation reaction (150 °C, 12 h) under autogenous pressure, giving 85.4% conversion of acrylonitrile to 3-methoxy-propionitrile. X-type zeolites (FAU topology) with different alkali metal cations (Li^+, K^+, Cs^+ and Ca^{2+}) were prepared *via* ion exchange where BLA was used as the silica source. As expected, zeolite CsX with the strongest basicity showed the best catalytic performance in the cyanoethylation of alcohols. The results indicated that the surface basicity of zeolite X framework gradually increases in the order of LiX < NaX < CaX < KX < CsX. Among the catalysts prepared, CsX with the most basic feature gives the best catalytic performance (97.0% conversion) in the cyanoethylation reaction study (9 h, 150 °C, autogenous pressure) whereas moisture sensitive CaX (28.2%) shows the poorest performance under the same reaction condition.

CHAPTER 1

INTRODUCTION

1.1. General introduction

Bamboo is a tribe of flowering perennial evergreen plant in the grass family of Poaceae and in the subfamily of Bambusoideae. Bamboo is recognized as the fastest growing plant in the world. It is an abundant, inexpensive and renewable resource. Bamboo related industries produce about 190k tons of waste per year [1]. The bamboo leaf itself has no commercial value and it is usually disposed by open burning, thus causing environmental pollution and disposal problems. The bamboo leaf contains 13–41 wt% of silica depending on the species, age, climate and geographical influences [2]. Other constituents in bamboo leaves are cellulose, hemicellulose, lignin, and trace amount of metals such as Al, Mg, Na, and Ca [3]. Thus, with such a large silica content in the leaf, proper use of this silica would contribute in circumventing environmental issues and the valorization of agricultural waste.

Zeolites are hydrated crystalline porous aluminosilicates. They are highly efficient catalysts in petrochemical applications, and also are typically used as supports for exotic catalysts (e.g. silver, palladium and platinum) [4]. So far, there are 235 types of framework structures have been synthesized and approved by the International Zeolite Association (IZA) [5]. The zeolite frameworks are built on an infinitely extending three-dimensional network of tetrahedral SiO_4 and AlO_4 units, which are linked to each other by sharing oxygen atoms. The framework contains channels or interconnected voids, which are in the micropore range. These voids are occupied by water molecules and cations (mainly alkali or alkaline earth metal ions) which counter-balance the negative charge of the framework [6].

Typical synthesis of zeolite uses sodium silicate or colloidal silica solution as a silica source. Over the past 20 years, there is an increased interest on the preparation of zeolites using agricultural wastes such as rice husk ash (RHA) and sugarcane bagasse ash (SBA) as the silica sources. In the most cases, harmful and expensive organic templates are added to the synthesis gel precursor as structure directing agents (SDAs) to direct the formation of a specific crystalline framework and to control the crystallite size of the zeolite materials [7]. After the synthesis, the organic template is removed *via* high temperature calcination [8] or Fenton-liked oxidation [9]. On the other hand, the adjustment of morphology, purity, crystallite size and chemical composition of zeolites can be done by manipulating the crystallization conditions such as seeding, aging time, stirring, and heating time [10, 11].

Bamboo leaf ash has enormous potential as a precursor in zeolite syntheses because of its high silica content. Unlike rice husk ash which has been widely used in the synthesis of nanoporous materials, the use of BLA in zeolite synthesis, however, is still not widely reported. BLA as a new renewable silica source for the synthesis of the variety of zeolite materials is a task of priority. Thus, the development and optimization of high quality of amorphous agro-silica source will have a tremendous impact on microporous materials syntheses.

Preparation of zeolites involving SDAs is generally expensive and, therefore, their use in environmental remediation is restricted. Cost limitations can be overcome by using low-cost raw materials for zeolite synthesis like BLA. Compared to traditional zeolite synthesis, BLA is used as a cheap silica source instead of expensive and harmful ethyl orthosilicate (TEOS), methyl orthosilicate (TMOS), water glass or fumed silica, and hence, it is considered as a cheap, eco-friendly and sustainable silica source.

For the zeolite synthesis using BLA system, the crystallization process might be different from the conventional system as the zeolite formation can be affected by many factors such as sources of silica and alumina used, crystallization time, synthesis temperature, type of SDA, and pH of the solution. Thus, a comprehensive study on the zeolite synthesis using BLA silica source is worth to be further explored. In addition, this study is also dedicated on zeolite synthesis free of organic SDAs (or template) for approaching the target of green chemistry. The synthesized zeolites are then used as basic catalysts for cyanoethylation of alcohols reaction.

1.2. Research objectives

The aim of this research is:

1. To prepare pure amorphous silica from bamboo leaves that can be used for the synthesis of zeolite microporous materials.
2. To synthesis and characterization of two types of zeolites: LTA-type zeolite and X-type zeolite.
3. To study the catalytic properties of synthesized zeolites in cyanoethylation of alcohols reaction.

1.3. Scope of thesis

This thesis consists of five chapters, which clearly explains the background, experimental and research findings of the project. Chapter 1 is an introduction describing the potential use of BLA in the synthesis of zeolite microporous materials. Chapter 2 is a comprehensive literature review elaborating the background of the use of agricultural silica in zeolite synthesis, fundamentals concepts of zeolite formation and the application of zeolites in heterogeneous catalysis.

Chapter 3 reports the synthesis of LTA-type zeolite from BLA. Prior to zeolite synthesis, silica ash is extracted from bamboo leaf using nitric acid treatment followed by combustion treatment (600 °C). Next, various synthesis conditions by manipulating the reaction time, reaction temperature, the concentration of Na_2O, water and SiO_2/Al_2O_3 ratio are considered for the synthesis of LTA-type zeolite.

Chapter 4 focuses on the study of the catalytic behavior of solid base zeolite X in the presence of different types of extra-framework cations. The Na^+ extra framework cations of zeolite X are ion exchanged with different basic cations (Li^+, K^+, Cs^+ and Ca^{2+}). The basic strength of these solids is further characterized by IR spectroscopy of adsorbed pyrrole. Evaluation of their catalytic performance, in the Cyanoethylation of alcohols, providing opportunities for the preparation of more efficient zeolite base catalysts. Furthermore, the zeolite catalyst recyclability test is performed.

Chapter 5 presents the summary of research findings and conclusion of this project. Recommendation for future works of this research work is also proposed to broaden the prospect of using the BLA agro-waste as an important silica source for the synthesis of nanoporous materials, and zeolite itself can also be used in other applications.

CHAPTER 2

LITERATURE REVIEW

2.1. Agricultural waste as amorphous silica source

Agricultural activities produce a large quantity of waste. This agro-waste attracts widespread attention for renewable energy generation. Many agricultural wastes such as oil palm, rice husk, sugarcane bagasse, bamboo leaf and corn leaf are considered as the potential raw materials for preparing high-valued products. The combustion of herbaceous biomass usually produces silica-rich ash where this ash has no commercial value [12]. Thus, it is urgently needed to explore the potential use of agricultural ash in materials synthesis and industrial applications.

Silica source plays an important role in zeolite synthesis. Hence, the purity of silica is of priority. Recent study showed that the purity of agricultural silica ash can be enhanced by pre-treating the ash in acid (HNO_3 or HCl) followed by air combustion at 600 °C for 2 h [13]. In addition, silica can also be extracted by using alkaline fusion approach at 550 °C with an alkali:ash ratio of 1[14]. This method can increase the silica content in ash up to 92 wt%.

Rice husk ash (RHA) is an important source to produce silica source. It has high silica content which is sufficient as a raw material to produce various types of crystalline and amorphous silica compounds [15]. Pre-treatment of rice husks *via* leaching in solutions of H_2SO_4, NaOH, NH_4OH, HCl and HNO_3, followed by thermal treatment at high temperatures ranging from 500 to 700 °C for various time intervals, has been proven as an effective route in removing most of the metallic impurities and producing white ash with high percentage of silica content [16−19]. For example, combustion of pre-treated rice husk at 700 °C for 6 h can increase the percentage of silica from 72.1 wt% to 94.95 wt% [20]. During the combustion, a temperature below 700 °C is preferable to avoid any transformation of amorphous to crystalline form [21].

2.1.1. Bamboo leaf ash

Bamboo leaves is one of the major agricultural wastes. It is a fibrous material containing cellulose as the major constituent, lignin and ash. The large amount of silica freely obtained from this source provides an abundant and cheap alternative of silica for many uses such as for cement substitute [22] and also to produce metallurgical silicon [23]. Bamboo leaf fired in an open atmosphere and then heated at 600 °C for 2 hours in a furnace was found with 75.9 wt% of amorphous silica [24].

As the main component in the bamboo leaf ash is the silica, it can be used as an added component in cement sand bricks and could be seen as a potential low cost building element. Burning the leaf into ash under controlled conditions and milling, turns it into a powdery siliceous material that may be used as an aggregate in making bricks and blocks. The bamboo leaf ash is formed by silica with a completely amorphous nature and a high pozzolanic activity [25].

2.2. Zeolites

Zeolite is a highly porous and low-density material composed of silicon, aluminum and oxygen atoms. The atoms are linked to create well-defined channels and cavities molecular frameworks (Figure 2.1) [26]. Stilbite is the first zeolite material discovered over 200 years ago by A. Crönstedt, a Swedish mineralogist in 1756. He named the new type of mineral "zeolite" (meaning as boiling stone in Greek word) as the zeolite containing stones released water and it is seemed boiling in water [27].

An empirical formula of a zeolite is represented in Equation 2.1:

$$M^{n}_{x/n}[(AlO_2)_x \bullet (SiO_2)_y] \bullet mH_2O \qquad \textbf{[Equation 2.1]}$$

where M represents the exchangeable cation of valence *n*. M is generally a Group I or II cation. The negative charge created by the Al atoms in the structure is balanced by these cations (extra-framework cations). These cations are added either during the synthesis or through the ion exchange post-synthesis treatment. The value of *x* is equal or greater than two, as alumina tetrahedron does not occupy adjacent tetrahedral sites. The value *m* represents the degree of hydration. The structural formulae of zeolites are usually determined based on the crystallographic unit cell.

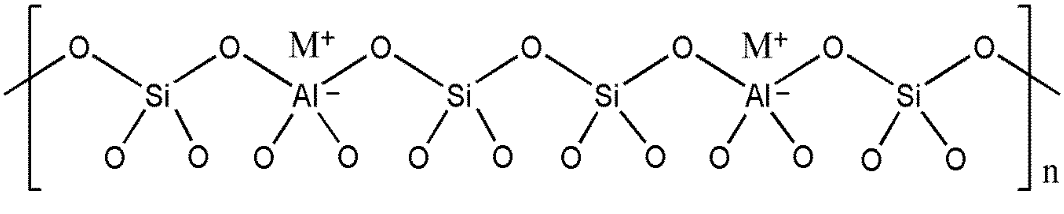

Figure 2.1. The basic chemical structure of zeolite framework, where Al sites present negative charge balanced by positively charged metal cations (M^+).

About 40 types of natural zeolites such as analcime, chabazite, clinoptilolite, erionite, ferrierite, mordenite, and phillipsite have been discovered during the past 200 years [28]. The zeolites which are important for industrial applications, however, are only synthesized after 1940s. The connectivity of the zeolite SiO_4 or AlO_4 tetrahedra gives rise to several millions of theoretically possible frameworks, of which are 235 types of framework structures have been synthesized experimentally and confirmed by the International Zeolite Association (IZA) [5]. The most common and commercially important zeolite materials are zeolites type A, X, Y, L and ZSM-5 [29].

Zeolites are typically classified by their pore size and composition. The size of the pores is typically expressed as the number of Si or Al atoms on the smallest possible cross-section, e.g. 8, 10, or 12 membered rings (MRs). Alternatively, they can be categorized by their Si/Al ratio, forming four classes: low, intermediate, and high Si/Al ratio zeolites, and all-silica zeolites (Table 2.1).

Table 2.1. Category of zeolites [30].

Zeolite grade	Si/Al molar ratio	Common mineral names with framework codes
Low silica	≤ 2	Analcime (ANA), cancrinite (CAN), Na-X (FAU), natrolite (NAT), phillipsite (PHI), sodalite (SOD), NaA (LTA)
Intermediate silica	2 – 5	Chabazite (CHA), faujasite (FAU), mordenite (MOR), NaY (FAU)
High silica	> 5	ZSM-5 (MFI), zeolite-β (BEA)
All silica	> 100	Silicate-1 (MFI)

2.3. Zeolite framework structures and properties

2.3.1. Linde type A (LTA)

Zeolite NaA was first synthesized in 1959 [31]. Zeolite A is one of the most widely used zeolites due to its high ion-exchange capacity and capability. Zeolite A has a framework type code known as LTA (Linde-Type A) consisting of sodalite (SOD) cages linked *via* four double four rings (D4R) [6]. As a result, an α-cage with a pore diameter of 12.3 Å and two channel systems which are inter-connected are produce to allow mobility of guest molecules (Figure 2.2) [32]. Its empirical formula is $Na_{12}[Al_{12}Si_{12}O_{48}]\cdot 27H_2O$ where the Si/Al ratio is usually 1.

Zeolite NaA has a high demand in detergent industry and it contributes about one million tons per annum in global synthetic zeolite market share [34]. Zeolite NaA is used as a water softening agent or so-called builder in laundry detergent. In addition, this zeolite is also important in wastewater treatment and purification processes [35].

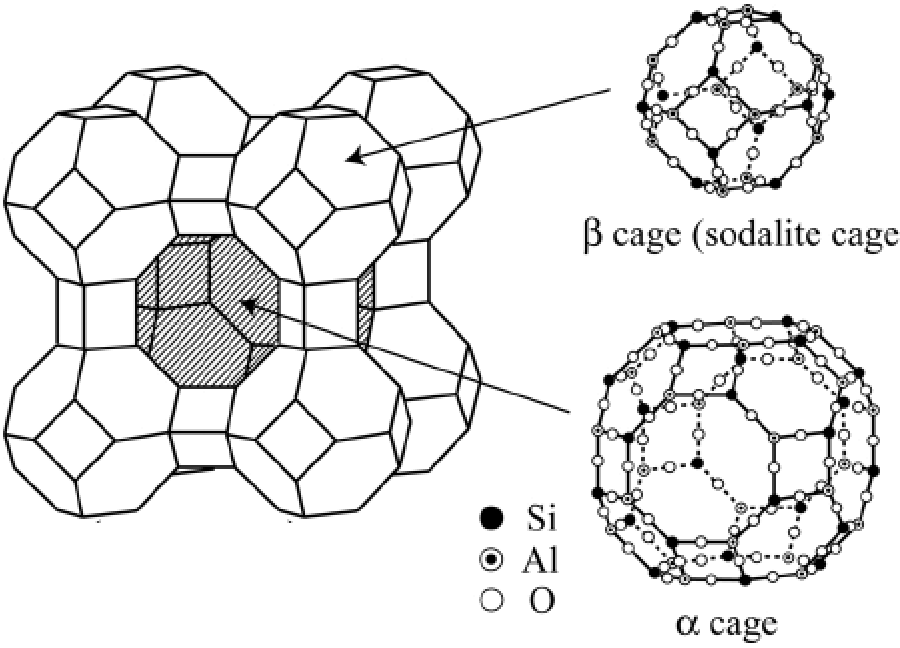

Figure 2.2. LTA-type zeolite structure with 3-dimensional pore channel system [33].

Conventional synthesis of zeolite NaA involves hydrothermal crystallization of aluminosilicate gels or solutions in the presence of sodium cations under alkaline environment (pH 14). Zeolite NaA can be synthesized using a variety of Al and Si sources, including aluminum, aluminum hydroxide, sodium aluminate, sodium silicate, silica gels, and reactive amorphous solid silica [36]. Recently, cheaper raw materials (such as clay materials [37], natural zeolites [38], coal ashes [39], municipal solid waste incineration ashes [40] and industrial slags [41]) consisted of Si or Si-Al elements are also used for industrial production of zeolite NaA [42]. On the other hand, zeolite NaA can also be synthesized using agro-waste ash such as rice husk ash [43−46] and sugarcane bagasse ash [47].

2.3.2. Linde type X and Y (faujasite, FAU)

The structure of faujasite was established for the first time by Bergerhoff et al. in 1956 [41]. The structure was then refined by Baur in 1964 [48]. Zeolites X and zeolite Y belong to the FAU family which consist of sodalite (SOD) cages linked *via* hexagonal prisms (Figure 2.3). Their basic unit cell comprises of eight sodalite cages and sixteen double six rings (D6Rs), which are connected to form a large spherical supercage [49]. This supercage structure (7.3 Å) provides the most open three-dimensional zeolite structure [50]. The empirical formula of zeolites X and Y can be represented by $Na_x[Al_xSi_{192-x}O_{384}]\cdot 220H_2O$ where for zeolites X and Y, the x value is in the range of 68−96 and 1−97, respectively.

Zeolite X was first using the newly discovered alumina-silicate gel method by Milton [52]. Today, zeolite X is widely used as the ion exchanger for water treatment due to its high ion exchange capacity and large pore size (7.3 Å) which enables it to scavenge the large hardness ions such as hydrated magnesium and iron ions [53, 54]. Faujasite type zeolite also has great catalytic properties particularly in the cracking of hydrocarbons. The presence of Brönster and Lewis acid properties made it a very important catalyst in the petrochemical industry [55].

Typically, an organic template such as tetramethylammonium (TMA^+) cation is used as a structure directing agent (SDA) for FAU crystals formation [56]. However, the use of organic template has several drawbacks. The organic templates, which are used in the synthesis, normally are environmentally unfriendly, toxic, non-recyclable and expensive [57]. Thus, any effort to synthesize faujasite zeolites free of organic template is highly appreciated.

The first zeolite X crystals synthesized from agricultural ash (rice husk ash) was reported in 1985 [58]. Since then, the development of rice-husk-synthesized zeolite X increased rapidly and the optimization study of the synthesis conditions has been reported to enhance the quantity and quality of the zeolites prepared [59, 60].

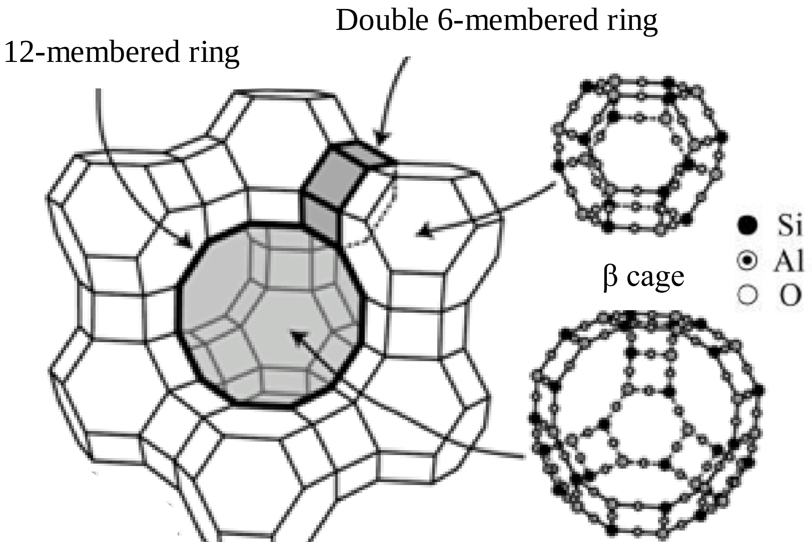

Figure 2.3. Framework structure of Faujasite zeolites (X and Y) [51].

2.4. Zeolite synthesis and formation

The most common method of zeolite synthesis is hydrothermal process under moderate temperature (< 250 °C) and pressure. It involves a synthesis precursor makes up of a basic salt (e.g. NaOH or KOH), water, silica and alumina sources [61]. Basically, the reactants for the source of alumina are generally sodium aluminate, aluminum nitrate, or aluminum hydroxide. For the source of silica, sodium silicate, amorphous silica, or silica sol are mainly utilized. In some cases, organic structure directing agent (SDA) is added in order to direct selectively the formation of desired zeolite framework structure.

The precursor reaction gel composition has little resemblance to the chemical stoichiometry of the final zeolitic product. The gel phase is formed by mixing silicate and aluminate solutions, at basic pH, in which the source of silicon and aluminum is either in a polymeric or monomeric form [62]. This synthesis mixture is then placed in a polypropylene (PP) bottle (for synthesis < 100 °C) or an autoclave (for synthesis < 250 °C) for hours, days or weeks which allow zeolites to crystallize out from the mother solution. The nature of zeolite (e.g. crystalline phase, size, morphology and porosity) is determined by the nature of reactants (silica and alumina sources), chemical composition, pH of the precursor, temperature, pressure, and organic template [63, 64]. The functions of reactants in the synthesis of zeolites are summarized and listed as in Table 2.2.

Table 2.2. Chemical sources and their functions in zeolite synthesis [65].

Sources	**Functions**
SiO_2	Primary building units of the framework
Al_2O_3	Origin of framework charge
OH^-, F^-	Mineralizer, guest molecule
Alkali cation, template	Counter ion of framework charge, guest molecule
H_2O	Solvent, guest molecule

After the reaction mixtures achieve the reaction temperature, the reactants sometimes remain amorphous where this stage is called induction period. The zeolite formation begins from the hydrous aluminosilicate amorphous gel when nucleation occurs. The careful controlled condition of the crystallization process gradually transforms all the amorphous phase into the desired crystalline zeolite phases [66]. The resulting zeolite particles after completion of crystallization process are removed from the mother liquor *via* filtration or centrifugation, washed until pH 7, and dried before any application. The steps involved in zeolite synthesis are summarized in Figure 2.4.

In order to make the synthesis process industrially important, the zeolite synthesis must have high reproducibility and the zeolite products must have the same specification each time. This aims to develop exact conditions for product optimization. The use of sodium silicate solution or solid sodium aluminate not only benefits in terms of cost and ease of operation, but also offers optimum synthesis routes to particular zeolite materials [67].

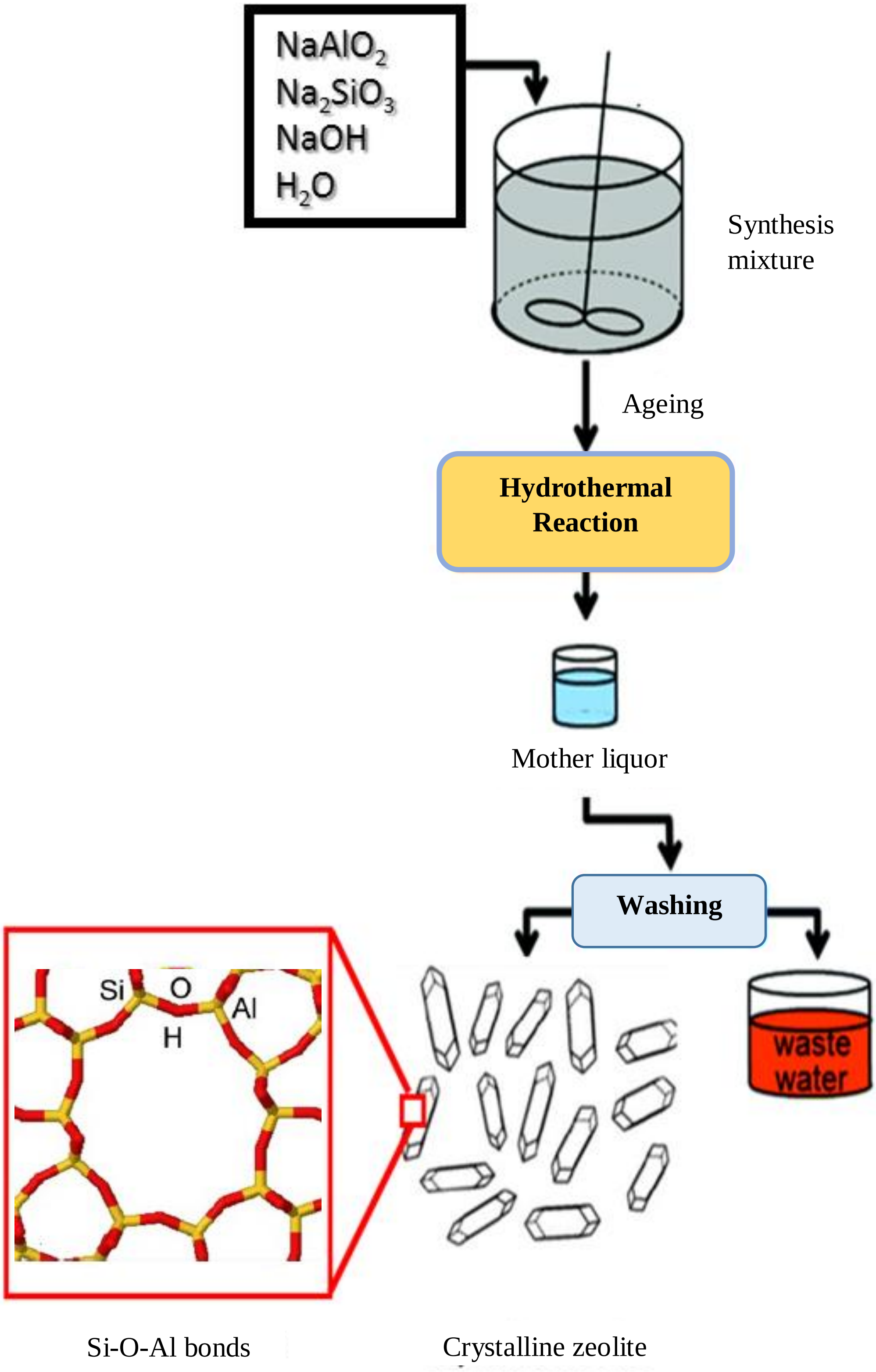

Figure 2.4. Hydrothermal zeolite synthesis process [67, 68].

2.5. Zeolite Catalysts

The exceptional performance of zeolites in catalyzed reactions stems from their strong acidity and uniformly-sized micropores [69, 70]. These properties enable to catalyze a wide variety of chemical conversions, while yielding very narrow product distributions [71]. The latter originates from the phenomenon known as "shape selectivity", that is, the limitation of the conversion of reagents into specific products caused by zeolite micropores [72]. Distinguish between various types of shape selectivity, depending on whether the aperture limits the inlet of the reaction molecule, the deviation of the product molecule, or the formation of certain transitions (Figure 2.5). These special catalytic characteristics by adjust the acidity and pore size, make the role of zeolite in catalysis indispensable.

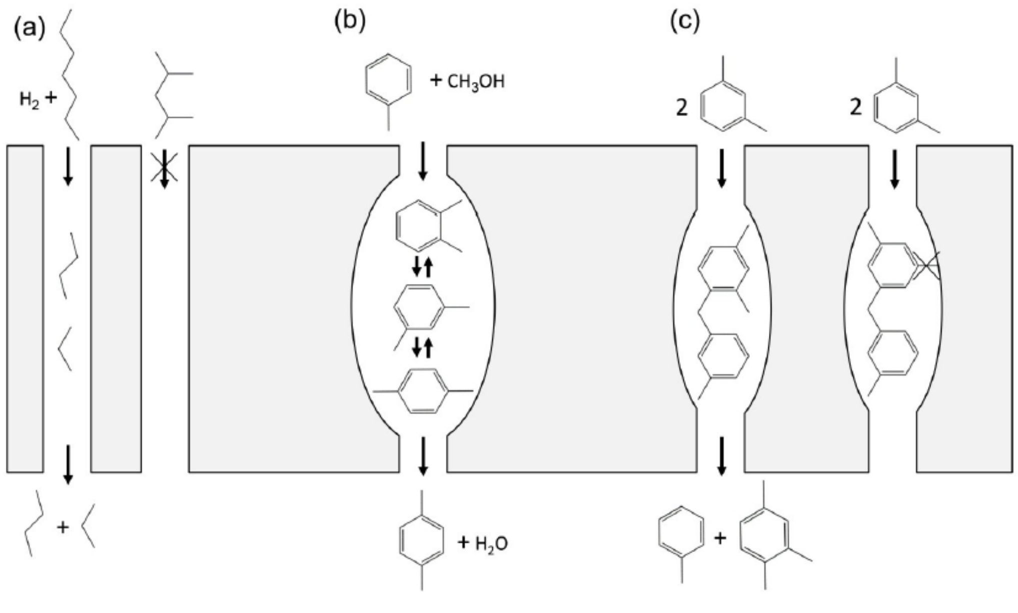

Figure 2.5. Types of shape selectivities occurring during zeolite-catalyzed reactions. Reaction selectivity (a) occurs when only part of the reactant molecules are small enough to enter the pores. Product selectivity (b) occurs when some of the products formed within the micropores are too bulky to diffuse out of the micropores. Transition

state selectivity (c) occurs when certain reactions are prevented because the corresponding transition state requires more space than is available in the cavities [73].

Although zeolites have achieved significant success as solid catalysts, their potential can only be exploited in part due to diffusion and access limitations. The limited size of the micropores with respect to the size of the molecules enforces an intra-crystalline diffusion. As a result, only the part of the micropores close the external surface is used in most catalyzed reactions.

2.6. Catalysis

Catalyst is defined as a substance that speeds up the reaction rate *via* offering another route with lower activation energy. In most cases, the catalysts do not undergo chemical change after the reaction [74]. Catalysts can be classified into two large groups: homogeneous and heterogeneous catalysts. Homogeneous catalyst is referred as the catalyst that exists in the same phase as the reactants (e.g. $AlCl_3$, HCl and H_2SO_4) whereas heterogenous catalyst is a catalyst which has a different phase from the reactants (e.g. zeolites, metal oxides, metals).

Heterogeneous catalysis is the backbone of the modern chemical industry, because of the necessity to achieve environmental benign processes in the industry. Although heterogeneously catalyzed processes are broadly used in petrochemical processes, most of the fine pharmaceutical and chemicals manufacturing processes still relies on the homogeneous catalysts which offer higher product yield. Nevertheless, heterogeneous catalysts offer numerous advantages over homogeneous catalysts, such as simple procedures, easy to handle and store, easy catalyst separation from the reaction mixture, low waste disposals and high catalyst reusability [75−77].

2.6.1. Zeolites as heterogeneous catalysts

Zeolites can be attractive catalysts in most of the applications due to their very stable framework structures against high temperature, high pressure, and reactive chemicals. The use of zeolites as catalysts basically depends upon the accessibility of reactants (size and shape) to the catalytically active centers located in the micropores. Specific catalytic actions of zeolites can be engineered *via* creating acidity or basicity on zeolite surface through ion-exchange with particular cations. For instance, acid sites (Brönsted acid and/or Lewis acid) can be created *via* ion exchange of NH_4Cl or NH_4NO_3 followed by calcination. On the other hand, basic sites are created through ion exchange of alkali cation (e.g. Cs^+, K^+, Ca^{2+}) salts [78].

2.5.2. Cyanoethylation reaction

Cyanoethylation is one of the common base catalyzed reactions. It involves reaction between acrylonitrile with different types of alcohols to form nitriles (Figure 2.5). Cyanoethylation is an important intermediate reaction in the preparation of alkoxypropionitriles, propanoamines and propionic acids where these products are important for the syntheses of drug intermediates and fine chemicals.

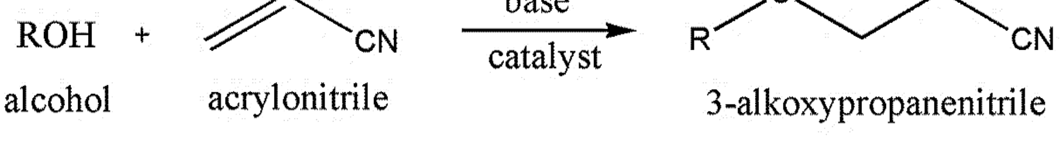

Figure 2.6. Cyanoethylation of alcohol with acrylonitrile to 3-alkoxypropanenitrile.

Classically, cyanoethylation of alcohols is catalyzed using homogeneous catalysts such as alkaline alkoxides, tetraalkylammonium hydroxides and alkali hydroxides [79]. However, homogeneous catalysts have limitation in most of the modern catalytic reactions due to the reusability problem. Recently, several literatures have reported the use of heterogeneous catalysts for cyanoethylation of aliphatic alcohols. Basic cation-exchanged zeolites such as Cs/Mg−modified zeolite Y are reported to be active in cyanoethylation of methanol and ethanol under microwave irradiation [80]. The results of the catalytic reaction under various reaction times and microwave powers are summarized in Table 2.3. The catalyst, however, is inactive when longer chain alcohol such as propanol is used. Based on the results, it can be seen that the reactivity of acyronitrile with alcohols decreases in the following order: methanol > ethanol > propanol.

Table 2.3. Conversion of acrylonitrile in the presence of modified zeolite Y catalyst (35.3% cesium, 9.1% magnesium) under microwave irradiation.

Power (W)	Conversion (%)					
	Methanol		Ethanol		Propanol	
	5 min	15 min	5 min	15 min	5 min	15 min
900	83	98	54	77	0	0
600	47	78	12	38	0	0
300	13	42	0	23	0	0

CHAPTER 3

LTA-TYPE ZEOLITE FROM BAMBOO LEAVES BIOMASS: EFFECT OF SYNTHESIS PARAMETERS AND ITS CATALYTICS ACTIVITY IN CYANOETHYLATION OF ALCOHOLS

3.1. Introduction

Zeolites are crystalline microporous materials which are commonly used as adsorbents, ion exchangers and catalysts [6]. While more than 235 types of zeolites are known today, only several types of zeolites are commercially available and used in industries. Particularly, zeolite A (LTA topology) has gained the most interest in industry and scientific community due to its accessible 3-dimensional pore opening and specific catalytic properties [81, 82].

Over the past few years, the use of agricultural wastes (e.g. rice husk ash [83−88] and sugarcane bagasse ash [40]) and industrial waste (coal fly ash [89–91]) as renewable silica sources for the preparation of various types of zeolites have been reported. Bamboo leaves, a biomass from agricultural industries are still under-utilized. There are about 190,000 tons of this agro-waste discarded annually, causing environmental problems when it is disposed on landfill or *via* open burning [1]. The potential of bamboo leaves as renewable silica source for the synthesis of inorganic ordered porous materials is very promising due to their high silica content (30–41%), high growth rate and practical consistencies [92]. Nevertheless, the extraction and use of the bamboo leaf silica for zeolite synthesis has not been reported and thus it is worth to be further explored.

In this chapter, we report for the first time the preparation of highly pure amorphous silica from bamboo leaves biomass for the synthesis of zeolite NaA. The effects of zeolite synthesis parameters (e.g. hydrogel chemical composition, synthesis time and heating temperature) are also carefully studied. Finally, the potential of zeolite A as a solid base catalyst in cyanoethylation of various alcohols reaction is demonstrated.

3.2. Experimental

3.2.1. Preparation of bamboo leaf ash (BLA)

Bamboo leaves were collected from USM campus. Dried Bamboo leaves (45.000 g) were first washed with tap water prior to cut into small pieces (ca. 3 cm), and treated with nitric acid (1.5 M, 1 liter, Qrëc) under agitation (90 rpm, 15 h). The acid-leached bamboo leaves were filtered and washed with distilled water until pH 7. The leaves were air dried prior to blending into fine pieces. The leaves were combusted at 600 °C for 6 h with a heating rate of 1.0 °C/min. Pure white ash (99.37 wt%) was obtained after the combustion process (Figure 3.1).

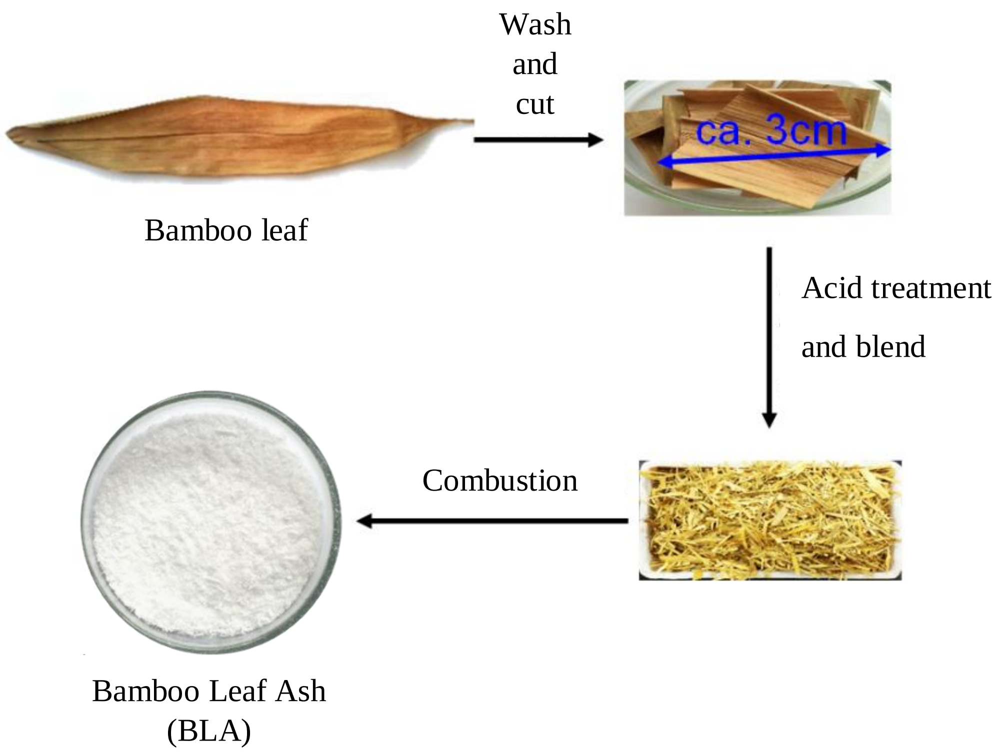

Figure 3.1. Procedure of preparation of bamboo leaf ash (BLA).

3.2.2. Synthesis of zeolite NaA

The synthesis experiment was carried out as follows: NaOH (10.094 g, Merck) and BLA (2.500 g) were added into a polypropylene (PP) bottle containing distilled water (71.676 g). The mixture was magnetically stirred (100 °C, 45 min) until the silica was fully dissolved. The aluminate solution was prepared by dissolving sodium aluminate (5.285 g, Sigma-Aldrich) and NaOH (0.294 g, Merck) in distilled water (76.620 g). The aluminate solution was then slowly added to the silicate solution under stirring. The resulting hydrogel, which had a final molar composition of $1.5SiO_2:1Al_2O_3:6Na_2O:300H_2O$, was stirred for another 10 min before putting into an oven at 90 °C for crystallization. The resulting solid product was filtered and purified with distilled water until pH 7 prior to drying at 90 °C overnight. The synthesis was also carried out by adjusting the reaction conditions and hydrogel chemical compositions using similar procedure. Detailed synthesis information and the reactant ratios were listed in Table 3.1.

Table 3.1. Chemical compositions of hydrogels and the zeolite synthesis conditions.

Effect of parameters	**Samples**	**Gel molar composition**				**T (°C)**	**t (h)**
		SiO_2	**Al_2O_3**	**Na_2O**	**H_2O**		
Time	A-1	1.5	1	6	300	90	1
	A-2						3
	A-3						5
	A-4						7
Temperature	A-5	1.5	1	6	300	70	7
	A-6					80	
	A-4					90	
	A-7					100	
Na_2O	A-8	1.5	1	2	300	90	7
	A-9			4			
	A-4			6			
	A-10			8			
SiO_2	A-11	1.0	1	6	300	90	7
	A-4	1.5					
	A-12	2.0					
	A-13	2.5					
H_2O	A-14	1.5	1	4	100	90	7
	A-15				200		
	A-4				300		
	A-16				400		

3.2.3. Characterization

The organic and inorganic component in bamboo leaf was investigated using a Mettler TGA SDTA851 instrument with a heating rate of 10 °C/min under air flow. The XRD patterns of samples were recorded on a Siemens D5000 Kristalloflex diffractometer (CuKα radiation, 4–40°, step size 0.01°, 2.0 s per step). The surface morphology of solid samples was evaluated by Nova NanoSEM™ field emission scanning electron microscope (FESEM) with an accelerating voltage of 20 kV. The mean and standard deviation of the size distribution of particles were determined by counting 50 particles randomly through FESEM observations obtained in different regions. FT-IR spectra were recorded using a Perkin Elmer System 2000 (4000-400 cm^{-1}, resolution 4 cm^{-1}, 32 scans). The elemental analysis of bamboo leaves was performed by using a Phillips X'Unique X-ray Fluorescence (XRF) spectrometer.

3.2.4. Cyanoethylation catalytic study

Cyanoethylation reaction was conducted as follows: Activated zeolite NaA (0.100 g, 400 °C, 5 h), methanol (76 mmol, 99.8%, Merck) and acrylonitrile (19 mmol, 99%, Merck) were added into a 15 mL Teflon container. The Teflon container was autoclaved and magnetically stirred in an oil bath at a desired temperature. Concurrently, the reaction was also performed in a 25 mL round bottom flask and heated under reflux on a stirring oil bath with ice-cold water being circulated through the condenser. The reaction solution was withdrawn and injected (0.2 μL) using a gas chromatograph (Agilent 7890A) equipped with a HP-5 capillary column and a FID detector. The identity of the product was confirmed by a GC-MS (Perkin-Elmer Clarus 600 system). The oven setting of the GC and GC-MS were shown in Table 3.1. The experiments were repeated for 3 times and the averaged conversion and its standard deviation were recorded. The conversion was calculated using the following equations where *n*-nonane was used as the internal standard:

$$\text{Conversion (\%)} = 100 - \left(\frac{\mathrm{A_{acry.}}}{\mathrm{A}_{n-\mathrm{nonane}}}\right)_{\mathrm{t_i}} \times \left(\frac{\mathrm{A}_{n-\mathrm{nonane}}}{\mathrm{A_{acry.}}}\right)_{\mathrm{t_o}} \times 100\% \quad \textbf{[Equation 3.1]}$$

where, $\mathrm{A_{acry.}}$ = Peak area of acrylonitrile, $\mathrm{A}_{n\text{-nonane}}$ = Peak area of *n*-nonane, $\mathrm{t_o}$ is the reaction time at time 0 hour, and $\mathrm{t_i}$ is the reaction at time i hour.

The reusability study of zeolite catalyst was performed as follows: zeolite solid was separated after the first reaction run. The solid was washed with diethyl ether, air dried and re-activated (400 °C, 5 h) before being used for the subsequent cycles of catalytic reaction. The reaction solution was separated again after the reaction and analyzed using GC.

Table 3.2. GC and GC-MS oven conditions.

Conditions	GC & GC-MS
Initial temperature (°C)	40
Initial hold time (min)	1
Ramp (°C/min)	17.5
Final temperature (°C)	250
Final hold time (min)	1
Carrier gas	Nitrogen