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Hydrothermal synthesis of zeolite a from bamboo leaf biomass and its catalytic activity in cyanoethylation of methanol under autogenic pressure and air conditions

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HIGHLIGHTS
- Amorphous bamboo leaf ash (BLA) with ca. 99% silica content was obtained.
- Zeolite A was synthesized from BLA silica.
- Various synthesis parameters of zeolite A were studied.
- The prepared zeolites gave 82% conversion in cyanoethylation of methanol.
- The catalyst is recyclable and active under autogenic pressure and air condition.

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ABSTRACT
We reported for the first time the use of bamboo leaf biomass (BLA) as a silica source for the synthesis of aluminosilicate zeolite A (structure code LTA). The BLA with very high silica purity (ca. 99%) was obtained from combustion of acid-treated bamboo leaves, a cheap and abundant agriculture waste. The formation of zeolite A from the BLA precursor was studied by varying the synthesis conditions, i.e. crystallization time, heating temperature and initial gel molar composition. The study revealed that the synthesis parameters had profound effects on crystalline phase, morphology and crystal size of the zeolite A produced. Moreover, this study also demonstrated that the BLA-synthesized zeolite A showed excellent catalytic performance in solvent-free cyanoethylation reaction of methanol under moisture-tolerant and autogenic pressure conditions, with ca. 82% reactant conversion and 100% product selectivity even reused up to ten reaction cycles.

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1. Introduction

Bamboo is a tribe of flowering perennial evergreen plant in the grass family of Poaceae and subfamily of Bambusoideae [1]. It is one of the fastest growing plants in the world with growing rate ranging from 30 to 100 cm day\(^{-1}\) during growing season [2]. Recently, bamboo is rapidly rising as a highly renewable resource because it is cheap, plentiful and easy to cultivate. Every year, there are almost 20 million tons of bamboo produced all over the world, mainly in Asia and Latin America, which generates 190 kilotonnes of bamboo leaves as waste [3]. The bamboo leaves have no commercial value and are usually disposed by open burning, thus causing environmental problems. Bamboo leaves were claimed to contain 13-41 wt% of silica depending on the species, age, climate and geographical influences [4]. By proper utilization of this silica-rich biomass, valorization of this agricultural waste will be possible and consequently will help in circumventing the related environmental issues.

Zeolites are crystalline microporous materials which are commonly used as adsorbents [5,6], ion exchangers [7] and catalysts [8–13]. While more than 235 types of zeolites are known today, only several types of zeolites are commercially available and used in industries [14]. Particularly, zeolite A with Linde Type 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 [15]. Over the past few years, the use of agricultural wastes (such as rice husk ash [16–19] and sugarcane bagasse ash [20]) and industrial waste (coal fly ash [21–23]) as renewable silica sources for the preparation of various types of zeolites and nanoporous materials have been reported. Nevertheless, the extraction and use of the bamboo leaf-based silica for zeolite synthesis has not been reported. Thus, any effort in using biomass for the synthesis of nanoporous catalyst materials is highly appreciated.

On the other hand, cyanoethylation is a reaction that involves an addition of acrylonitrile to compounds with reactive hydrogen (e.g. alcohols). It is a versatile reaction for synthesizing a variety of useful pharmaceutical and fine chemical compounds [24]. Previous study has reported that this reaction is very moisture sensitive and must be performed under inert atmosphere in the presence of a basic catalyst [25]. There is an urgent need for cyanohydrination to be carried out with greener methodologies, for instances, at ambient air condition. In this paper, we report for the first time the extraction of highly pure amorphous silica from bamboo leaves biomass for the synthesis of zeolite A. The effects of zeolite synthesis parameters, i.e. initial hydrogel chemical composition, synthesis time and heating temperature are then carefully studied. Furthermore, the potential of zeolite A as a solid base catalyst in cyanoethylation of various alcohols with acrylonitrile under autogenic pressure and in the presence of water is also demonstrated. The surface basicity of zeolite A is first studied before the catalytic reaction is optimized with various reaction parameters such as reaction time, temperature and molar ratio of reactants before the catalyst reusability was performed.

2. Experimental

2.1. Preparation of bamboo leaf ash (BLA)

Bamboo leaves were taken directly from a nearby bamboo factory. Bamboo leaves (45,000 g) were first washed with distilled water prior to cut into small pieces (ca. 3 cm), and treated with nitric acid (1.5 M, 1 L, Qréc) under agitation (90 rpm, 15 h) at room temperature. The acid-leached bamboo leaves were filtered and washed with distilled water until pH 7. The leaves were air dried at room temperature 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 (31.7% yield) was obtained after the combustion process. For comparison study, the bamboo leaves without preliminary acid treatment were also combusted under similar condition.

2.2. Synthesis of zeolite A

The synthesis experiment was carried out as follows: NaOH (10.094 g, Merck) and BLA (2.500 g) were added into a polypropylene bottle containing distilled water (71.676 g). The mixture was magnetically stirred at 100 °C for 45 min. 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\(_2\)O\(_3\):6Na\(_2\)O:300H\(_2\)O, 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. Other syntheses were also carried out by varying the reaction conditions and hydrogel chemical compositions using the similar procedure. The details of the syntheses were summarized in Table 1.

2.3. Characterization

Thermal gravimetric analysis (TGA/DTG) on the bamboo leaves was investigated using a Mettler TGA SDTA851 instrument with a heating rate of 10 °C/min under air flow (100 mL min\(^{-1}\)). The XRD patterns of the samples were recorded on a Siemens D5000 Kristalloflex diffractometer (CuK\(_\alpha\) radiation, 5–40°, 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. The elemental analysis of bamboo leaves was performed by using a Phillips X’Unique X-ray Fluorescence (XRF) spectrometer. The surface basicity of zeolite A

<table>
<thead>
<tr>
<th>Effect of parameters</th>
<th>Samples</th>
<th>Gel molar composition</th>
<th>T (°C)</th>
<th>t (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>A-1</td>
<td>1.5 1 6 300 90 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-2</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>A-3</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-4</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-5</td>
<td>1.5 1 6 300 70 7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-6</td>
<td>80</td>
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<tr>
<td>A-7</td>
<td>90</td>
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<tr>
<td>A-8</td>
<td>100</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>A-9</td>
<td>4</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>A-10</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-11</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Temperature          | A-8     | 1.5 1 2 300 90 7     |
|----------------------|---------|-----------------------|--------|-------|
| A-9                 | 4       |
| A-10                | 6       |
| A-11                | 8       |
| A-12                | 100     |
| A-13                | 200     |
| A-14                | 300     |
| A-15                | 400     |
| A-16                | 7       |
was studied using a CO₂-TPD analyzer (AutoChem II 2920). Initially, the sample was degassed at 500 °C for 6 h before CO₂ was introduced and adsorbed onto the sample. The sample was then heated up to 900 °C at 10 °C min⁻¹.

2.4. Cyanoethylation catalytic study

Prior to catalytic testing, the water content in the methanol (98%, Merck) and acrylonitrile (99%, Merck) was measured using a volumetric Karl Fischer titrator. The Karl Fischer titration system (Metrohm) was charged with Hydranal Composite-2 reactant (Riedel-de Häan) and Hydranal Solvent CM (Riedel-de Häan). Both reagents were analyzed twice to obtain average values by direct injection without preliminary treatment.

Cyanoethylation reaction was conducted as follows: Activated zeolite A (0.100 g, 400 °C, 5 h), methanol (76 mmol) and acrylonitrile (19 mmol) were added into a 15 mL Teflon container. The Teflon container was autoclaved and magnetically stirred in an oil bath at a desired temperature. At the end of the reaction, the zeolite catalyst was recovered from the reaction product by filtration. For quantification, a 0.2-μL of reaction product was then injected into a gas chromatograph (Hewlett-Packard 5880) equipped with a HP-5 capillary column and a FID detector; nitrogen was used as carrier gas. The identity of the product was confirmed by a gas chromatography–mass spectrometer (Perkin-Elmer Clarus 500 system). 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 an internal standard:

\[
\text{Conversion} = 100 - \left[ \left( \frac{A_{\text{acrylonitrile}}}{A_{\text{n-nonane}}} \right)_{t_n} \times \left( \frac{A_{\text{n-nonane}}}{A_{\text{acrylonitrile}}} \right)_{t_0} \right] \times 100
\]

where \( A \) is the peak area, \( t_0 \) is the initial reaction time (at 0 h) and \( t_n \) is the final reaction time (at n h).

The reusability study of zeolite catalyst was performed as follows: the zeolite solid recovered after the first reaction run was washed with diethyl ether (20 mL, three times), air dried at room temperature and re-activated (400 °C, 5 h) before being used for the subsequent cycle of catalytic reaction. For each subsequent reaction run, the reaction product was analyzed using the aforementioned procedure.

3. Results and discussion

3.1. Bamboo leaves and bamboo leaf ash

Bamboo leaves contain both organic and inorganic moieties. Hence, TGA was used to study the thermal decomposition pattern of the organic moieties and to determine the non-combustible mineral content in the bamboo leaves. The thermogravimetry and differential thermogravimetry (TG/DTG) profiles of the bamboo leaves were shown in Fig. 1a. Three main steps of weight loss were identified: the first step (<160 °C) was due to water desorption, the second step (160–380 °C) was owing to decomposition of hemi-cellulose and cellulose and the third step was originated from decomposition of lignin [26]. The TG/DTG data showed that the bamboo leaves contained 31.7 wt% of non-combustible ash which was much higher than that of rice husk (~20 wt%) [27].

The XRF data of the ashes was shown in Table 2. For the bamboo leaves that did not receive preliminary nitric acid treatment, the ash contained 77.09% of SiO₂ and high content of inorganic impurities: K₂O (8.00%), CaO (5.96%), SO₃ (3.96%), P₂O₅ (2.13%), MgO (2.03%), etc. After acid treatment, the inorganic impurities were extracted and removed from the bamboo leaves. As a result, the inorganic moieties were significantly reduced to <0.26% and an increment of SiO₂ content in BLA to 99.37% was observed. Furthermore, no black carbon residue was observed in BLA further confirming the XRF data (inset of Fig. 1b). The XRD pattern of BLA exhibited only one broad hump, centered at 2θ = 23°, revealing the amorphous nature of the silica ash (Fig. 1b) [28].

3.2. Synthesis of zeolite A

The formation of zeolite A was followed at different heating times at 90 °C. The sample obtained after 1 h of hydrothermal heating was amorphous, and nanoparticles (ca. 126 nm) with no distinct morphology were formed according to the XRD and FESEM analyses (Fig. 2a). Of the various crystal growth mechanisms that have been proposed for the hydrothermal synthesis of zeolite A, formation of primary nanoparticles has been mutually recognized as the initial growth step [29]. The amorphous nanoparticles

![Fig. 1.](image)

**Fig. 1.** (a) TG/DTG profile of bamboo leaf and (b) XRD pattern of BLA ash after combustion. Inset: Physical appearance of BLA.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>XRF analysis of BLA with and without acid leached treatments.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Before treatment</td>
<td>77.09</td>
</tr>
<tr>
<td>After treatment</td>
<td>99.37</td>
</tr>
</tbody>
</table>

"bdl" — below of detection limit.
captured by the FESEM could be accredited to the primary nanoparticles. While the broad amorphous hump remained significant after 3 h of hydrothermal treatment, several diffraction peaks at 2θ = 7.14°, 10.18°, 21.76°, 24.04°, 27.17°, 32.02° and 34.20° which corresponded to zeolite A crystalline framework were identified (Fig. 2b) [30]. This suggested that nucleation process had been occurred. A few chamfered cubes with diameter less than 2 µm, which can be ascribed to zeolite A, were detected in the FESEM image (Fig. 2b). The zeolite A crystalline phase became dominant after 5 h of crystallization. More Cubic-shaped zeolite A crystals with truncated edges could be seen and the crystals had an average diameter of 1.92 ± 0.56 µm (Fig. 2c). The amorphous nanoparticles, however, were still detected in the FESEM image at this stage. With heating prolonged to 7 h, fully crystalline zeolite A in chamfered cubic shape was obtained without the presence of the primary nanoparticles (Fig. 2d). As shown, the diffraction peaks were strong, sharp and similar to the characteristic peaks of pure LI4 phase [30]. No diffraction peak corresponding to any other zeolitic phase and crystalline impurities was observed. Thus, this suggested that pure zeolite A with good crystallinity had been successfully synthesized using BLa as the silica source.

3.2.1. Effect of synthesis temperature

The activation energy of crystallization can be affected by heating temperature [31]. Thus, the hydrogels of a molar composition of 1.5SiO2: 1Al2O3: 4Na2O: 300H2O were heated separately at 70, 80, 90 and 100 °C for 7 h in order to study the effect of heating temperature (Table 1). The product was amorphous according to XRD analysis when the hydrogel was heated at 70 °C (Fig. 3a). Only agglomerates of nanoparticles were observed in the FESEM image. With temperature increased to 80 °C, the zeolite A crystalline phase became dominant (Fig. 3b). Both the chamfered cubes of zeolite A and the nanoparticles were detected in the FESEM image. The amorphous nanoparticles were slowly converted into zeolite A with an average crystal size of 1.72 ± 0.32 µm. Fully crystalline solids were obtained at 90 °C as evidenced by the XRD pattern and FESEM image (Fig. 3c). No amorphous nanoparticles was detected in the FESEM image. When the crystallization temperature was further increasing to 100 °C, co-crystallization of cancrinite and sodalite dense phases was detected with the presence of their characteristic diffraction peaks in the XRD pattern (Fig. 3d). Crystals with lepi-spheric morphology intergrown on top of the zeolite A cubic crystals were also observed in the FESEM image (Fig. 3d). Overall, the crystallization of zeolite A was temperature-dependent and was a thermally-activated process according to the XRD and FESEM studies. Hydrothermal treatment at 90 °C was used for the subsequent zeolite A syntheses reported hereafter.

3.2.2. Effect of Na2O content

Zeolite A crystals were also synthesized using different Na2O contents (Table 1). Except for sample A-8 (Fig. 4a) which was prepared with lowest Na2O content, all other samples consisted only of zeolite A chamfered cubes as shown in the FESEM images. From the XRD patterns depicted in Fig. 4, the intensities of the diffraction peaks were increased when higher Na2O contents were used. These results showed that the crystallization rate was enhanced with an increase of Na2O content, indicating the direct participation of soluble Na2O species in crystal growth process [32]. The average crystal sizes of the zeolite A samples were found similar (ca. 1.95 µm) irrespective to the Na2O content used. Nevertheless, the crystal size distribution (standard deviation of the average size) decreased with increasing the Na2O content. The results suggested that high Na2O content had enhanced dissolution of amorphous particles and hence generated reservoir of nutrients which was used for further growth of small crystals [33]. As a result, the standard deviation of size distribution decreased.

3.2.3. Effect of SiO2 content

The effect of the hydrogel SiO2/Al2O3 ratio (ranging from 1.0 to 2.5) on the crystalline end products was studied (Table 1). The XRD analysis revealed that all samples possessed pure zeolite A crystalline phase and no other competing phases such as zeolite NaX, hydroxysodalite and cancrinite were detected in the SiO2/Al2O3 range studied (Fig. 5). In addition, the average crystal size and crystal size distribution were not greatly affected by the hydrogel SiO2/Al2O3 ratio according to the FESEM analysis (Fig. 5). However, the morphology of zeolite A crystals changed upon varying the SiO2/Al2O3 ratio. The zeolite A crystals displayed a regular cubic morphology with sharp edges when the hydrogel of low silica content (SiO2/ Al2O3 = 1.0) was employed. With increasing the SiO2/Al2O3 ratio to 1.5 and 2.0, zeolite A crystals consisted of a mixture of cubic crystals of sharp and truncated edges were formed. At a SiO2/Al2O3 ratio of 2.5, the zeolite A produced was mostly chamfered cubes with truncated edges. Thus, a gradual shape evolution of zeolite A crystals from sharp-edged regular cubes to chamfered cubes could be realized by tuning the SiO2/Al2O3 ratio of the hydrogel. The results are in contrast to the work reported by Basaldella et al. [34] which studied the effect of initial hydrogel SiO2/Al2O3 ratio on crystal size and morphology of hydrothermally synthesized zeolite A. In their study, the SiO2/Al2O3 ratio was varied from 1.48 to 2.69 where Na/Si and H2O/Na2O ratios were kept as 1.01 and 53, respectively. It was reported that the particle size of zeolite A was increased (from 1.5 to 10 µm) by increasing the SiO2/Al2O3 ratio. At the same time, the morphology of the zeolite A crystals changed from chamfered cubic shape to regular cubic shape. When the experiment was repeated at Na/Si ratio of 0.58, similar results were obtained. In that study, a commercial kaolinite was used as both silica and alumina sources with a commercial sodium aluminate

![Fig. 2. XRD patterns and FESEM images of solids after heating for (a) 1 h, (b) 3 h, (c) 5 h and (d) 7 h.](Image)

![Fig. 3. XRD patterns and FESEM images of solids after heating at (a) 70 °C, (b) 80 °C, (c) 90 °C and (d) 100 °C for 7 h. The * and † marks indicate the presence of cancrinite and hydroxysodalite dense phases, respectively. The arrows shown in FESEM image indicate co-crystallization of cancrinite and hydroxysodalite phases.](Image)
used as a supplement when additional aluminum was needed.

In the current study, Na/Si ratio was varied from 4.8 to 12 while the H2O/Na2O ratio was kept as 50. The sodium cations in the current synthesis systems were much higher than that of the work performed by Basaldella et al. The large amount of sodium cations might favor the nucleation rate and selectively enhance the crystal growth along the [110] plane, hence producing chamfered cubic crystals. However, this selectivity might be disturbed by the presence of higher aluminum content (low SiO2/Al2O3) leading to the formation of regular cubic crystals, but with similar particle size. Chamfered cubic zeolite A crystals had also been obtained by other research groups when hydrogels with Na/Si > 2 and H2O/Na2O/C2150 were used [29,35]. In contrast, the influence of aluminum concentration on the nucleation rate became dominant when Na/Si/C201, such as in the work of Basaldella et al. A decrease of Al in the gel resulted in a lower number of nuclei formed and therefore leading to the formation of larger cubic crystals with sharp edges.

3.2.4. Effect of water content

The effect of water content in hydrogel was investigated by using the following composition: 1.5 SiO2: 1Al2O3: xNa2O: 300H2O with (a) x = 2 (A-8), (b) x = 4 (A-9), (c) x = 6 (A-3) and (d) x = 8 (A-10). The syntheses were performed at 90 °C for 7 h.

![Fig. 4. XRD patterns and FESEM micrographs of solids prepared using a hydrogel molar composition of 1.5 SiO2: 1Al2O3: xNa2O: 300H2O with (a) x = 2 (A-8), (b) x = 4 (A-9), (c) x = 6 (A-3) and (d) x = 8 (A-10). The syntheses were performed at 90 °C for 7 h.](image)

Chamfered cubic zeolite A crystals synthesized with low water content were broader than those of zeolite crystals obtained in higher water content. Such peak broadening could be explained by the small crystallites [36]. The XRD observation was fully supported by FESEM study where A-11 sample (y = 100) exhibited the smallest crystal size (1.11 ± 0.40 μm) whereas A-13 sample (y = 400) had the largest crystal size (2.12 ± 0.39 μm). A plausible explanation to this observation is that in a hydrogel with relatively low H2O content, the silicate and aluminate monomers and oligomers are easier to dissolve (due to high alkalinity), resulting in a high super-saturation solution, viz. a condition of having many nucleation sites. Thus, less nutrients are available for crystal growth and as a result, smaller zeolite A crystals were obtained at lower water content [37].

3.3. Catalytic study

3.3.1. Surface basicity characterization

CO2-TPD was used to characterize the surface basicity of zeolite NaA (A-4 sample). The study of the framework basicity is based on the bonding strength of CO2 with the basic sites of zeolite A (oxygen species) [38]. The CO2-TPD profile indicated the presence of three desorption peaks at ca. 78 °C, 182 °C and 340 °C which can be attributed to the interaction of CO2 with the sites of weak, medium and medium strong basic strengths, respectively (Fig. 7). Zeolite NaA did not show the desorption peak at high temperature. Hence, this confirmed the negligible presence of strong basic sites in this sample and it can be concluded that zeolite NaA is a mild basic solid catalyst.

3.3.2. Effects of catalyst and reaction time

First, cyanoethylation between acrylonitrile and methanol was
chosen as a model reaction. Acrylonitrile and methanol have a molecular size of $3.29 \times 3.34 \times 1.03 \text{ Å}^3$ and $2.35 \times 1.85 \times 1.83 \text{ Å}^3$, respectively, and it is expected that these molecules are able to diffuse and react in the micropores of zeolite A (pore diameter $3.84 \times 3.84 \text{ Å}$) [8,39]. In this study, zeolite A (A-4 sample) was used for the catalytic reaction study since the zeolite A samples prepared from different synthesis conditions were found to have almost identical catalytic performance (conversion $\pm 3.2\%$).

The cyanoethylation reaction was performed at 150 $^\circ$C using autoclave; the reaction solution contained 424 ppm of water according to Karl Fischer titration analysis. In the absence of zeolite A catalyst, no reaction conversion was observed (Fig. 8). Thus, this result supported previous observation that cyanoethylation reaction is a catalytic activated reaction [25]. With zeolite A as a catalyst, high conversion rate of 85.4% with 3-ethoxy-propionitrile as the only product was achieved within 12 h under autogenic pressure and air conditions. Cyanoethylation of methanol reaction, on the other hand, also took place under reflux condition but with a much lower conversion rate (48.7%) for a similar reaction time. Thus, this study indicated that high pressure exerted in the autoclave reactor promoted the reaction and increased the conversion rate of acrylonitrile as compared to the reaction run in reflux system.

In addition, cyanoethylation, which is a moisture-sensitive reaction [40], was also carried out in the presence of trace amount of moisture where water was found to be beneficial to the catalytic reaction. It is because a large number of OH groups, which is generated during rehydration of the thermally activated zeolite, is produced on the zeolite surface [41]. These groups act as Brönsted basic sites that can catalyze the cyanoethylation reaction.

3.3.3. Effect of reaction temperature

Cyanoethylation was also investigated at 30, 100, 120, 150 and 170 $^\circ$C in the presence of zeolite A catalyst (Fig. 9). At 30 $^\circ$C, both reflux and autoclave systems had similar conversion (ca. 3.7%).
When the reaction was performed in an autoclave at 100 °C, 100% selectivity to 3-methoxy-propionitrile was achieved at a moderate conversion level (21.6%). In contrast, only 9.8% of conversion was recorded when cyanoethylation reaction was performed using reflux method at the same temperature. As expected, the conversion rate, particularly for autoclave method, increased steadily as the temperature was raised from 100 to 150 °C (21.6%–85.4%). This is because high temperature increases the reaction system pressure which is important for the enhancement of the catalytic reaction rate. Cyanoethylation was also performed at 170 °C but without success due to degradation of the reactants; black solution was obtained after completion of reaction. Based on the results obtained, the optimum catalytic performance under autogenic pressure (highest conversion and highest selectivity to 3-methoxy-propionitrile) was achieved at 150 °C.

3.3.4. Effect of molar ratio of reactants

The molar ratio of acrylonitrile to methanol was varied from 1:0.5 to 1:8 with 0.10 g of catalyst at 150 °C using autoclave approach. The results obtained after 12 h of reaction indicated that the conversion of acrylonitrile was enhanced with an increase in the methanol amount (Fig. 10). Thus, this indicated a positive reaction order with respect to 3-methoxy-propionitrile. The highest percentage of conversion was achieved (~87%) at a molar ratio of acrylonitrile to methanol of 1:6 and remain constant for molar ratio of 1:8.

3.3.5. Effect of type of alcohols

Various alcohols were tested as the reaction substrate using autoclave method. Six types of alcohols containing aliphatic, cyclic and aromatic ring with different molecular sizes, namely methanol, ethanol, propanol, butanol, cyclohexanol and phenol, were selected and studied (Table 3). The results showed that zeolite A was active for small alcohol molecules (methanol, ethanol) and the catalytic activity decreased with increasing the molecular weight/size of alcohols. Such phenomenon is expected because only alcohols with small molecular size, such as methanol and ethanol are able to diffuse and react with acrylonitrile at the active sites, (Si-O-Al)–Na⁺, which are mainly available in the micropores of zeolite A (pore diameter 3.84 × 3.84 Å²) [8,32]. In contrast, larger molecules such as propanol, butanol, cyclohexanol and phenol were unable to diffuse into the micropores due to size constraint and hence little to no reactant conversion was observed after the reaction.

3.3.6. Catalyst reusability

Catalyst reusability is a major concern for solid catalysts in liquid phase reaction. Thus, a reusability study for zeolite A was conducted and the results showed that the catalyst could be recycled and reused. The zeolite catalysts was catalytic active for 10 successive runs without significant loss in activity (conversion ca. 82.8% and selectivity to 3-methoxy-propionitrile remained 100%) (Fig. 11). This suggested that the Na⁺ extra-framework cations were strongly bound to the zeolite surface and little to no leaching of these cations to the reaction solution occurred. Hence, the reusability test suggested that zeolite A synthesized from BLA silica can be used as a potential solid base catalyst for small molecules under

![Fig. 9. Effect of reaction temperature on cyanoethylation of methanol catalyzed by zeolite A catalyst under reflux and autogenous pressure conditions.](image)

![Fig. 10. Effect of reactant molar ratio on the conversion in cyanoethylation of methanol.](image)

<table>
<thead>
<tr>
<th>Type of alcohols</th>
<th>Molecular weight (gmol⁻¹)</th>
<th>Molecular size (Å³)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
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<td>2.35 × 1.83 × 1.85</td>
<td>85.4</td>
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<tr>
<td>Ethanol</td>
<td>46.06</td>
<td>3.69 × 1.79 × 2.00</td>
<td>21.6</td>
</tr>
<tr>
<td>Propanol</td>
<td>60.09</td>
<td>5.43 × 1.87 × 3.19</td>
<td>4.5</td>
</tr>
<tr>
<td>Butanol</td>
<td>74.12</td>
<td>5.95 × 1.87 × 3.21</td>
<td>0.7</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>100.15</td>
<td>5.07 × 4.31 × 2.82</td>
<td>0</td>
</tr>
<tr>
<td>Phenol</td>
<td>94.11</td>
<td>5.78 × 4.27 × 0.99</td>
<td>0</td>
</tr>
</tbody>
</table>

* The molecular size was estimated using HyperChem 7.0 software.
autogenic pressure besides its potential molecular sieving applications.

4. Conclusion

In conclusion, amorphous BLA with very high silica content (99.37%) have been successfully prepared from bamboo leaves after acid and combustion treatments. The BLA is found to be suitably used as the silica source for the hydrothermal synthesis of zeolite A. The synthesis parameters (e.g. hydrogel chemical composition, synthesis time and heating temperature) have been found to have significant effects not only on the average size and size distribution of the zeolite crystals, but also on the morphology and purity of the crystalline phase. From an environmental point of view, this work is extremely beneficial since BLA, which was derived from agricultural biomass, can be used as an alternative renewable silica source to synthesize other types of silica-based porous materials (e.g. zeolites, mesoporous materials, aerogels, etc.). Furthermore, the results also suggested that zeolite A synthesized from BLA can also be a promising solid base catalyst for small molecules in cyanoethylation reaction under autogenic pressure condition besides its potential molecular sieving and ion-exchange applications.

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References