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A series of alkali form (Na, K, Cs, and Ca) faujisite X-type zeolites were prepared from bamboo leaf ash, which was derived from bamboo agricultural waste. The XRD and SEM results revealed that the zeolite structure remained intact after ion exchange treatment. A very high degree of ion exchange ($\geq 85\%$) was achieved in all of the prepared zeolite samples. The zeolite samples were tested in a solvent-free cyanoethylation reaction of methanol under an instant heating environment that mimicked microwave fast heating, which was explored for the first time. The catalytic performances of the zeolite samples were well correlated with their surface basicity, which was characterised by pyrrole adsorption followed by in situ infrared spectroscopy. The CsX zeolite showed excellent catalytic performance ($\sim 97\%$ reactant conversion and 100\% product selectivity within 15 min), which was comparable to the microwave-assisted system and superior to the normal reflux system. The catalytic activity of the CsX zeolite was retained even after 10 cycles of reaction.

Introduction

Zeolites are a class of crystalline microporous materials, which have been widely studied for adsorption, ion exchange and catalysis applications.\textsuperscript{[1–3]} Nearly 230 types of zeolites are known today, but only a few of these types are commercially available and used in industry.\textsuperscript{[4]} Particularly, zeolite X with faujisite (FAU) topology has been extensively investigated and used as adsorbents,\textsuperscript{[5,6]} membranes,\textsuperscript{[7]} catalysts,\textsuperscript{[8,9]} and solid supports,\textsuperscript{[10]} due to its accessible three-dimensional pore opening, hydrophilic surface, high sorption capacity towards specific adsorbates, and good catalytic properties. Bamboo is one of the fastest growing plants on Earth.\textsuperscript{[11]} It is cheap, plentiful, renewable, and easy to cultivate. Every year, the global production of bamboo is $\sim 20$ million tonnes with $\sim 190$ kg tonnes of bamboo leaves generated as agricultural waste.\textsuperscript{[12]} Usually, the bamboo leaves are burned in open fields or dumped into landfills, thus causing environmental and pollution problems. Recently, many reports have been published on the use of agricultural wastes, such as rice husk ash (RHA)\textsuperscript{[13–16]} and sugarcane bagasse ash (SCBA),\textsuperscript{[17]} as silica sources for synthesising zeolite X. As bamboo leaves have a higher natural silica content (20–41\%)\textsuperscript{[18]} than RHA (14–25\% SiO$_2$)\textsuperscript{[19]} and SCBA (10–25\% SiO$_2$),\textsuperscript{[20]} the ash of this biomass could be an excellent candidate as a silica source. To the best knowledge of the authors, the use of bamboo leaf ash (BLA) for preparing microporous materials has not been reported so far. Hence, any effort to use BLA for zeolite X synthesis is worthy of further exploration.

Cyanoethylation is an important reaction in the field of organic chemistry to incorporate a cyanoethyl group into a molecule. It is a versatile reaction for synthesising a variety of useful pharmaceutical and fine chemical compounds.\textsuperscript{[21]} The cyanoethylation has to be performed under moisture-sensitive and inert atmospheres if solid basic catalysts are used.\textsuperscript{[22]}

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However, it has recently been reported that this reaction performs well in an Na$_2$CO$_3$ weak alkaline aqueous solution (homogeneous catalytic system).

In this work, we report for the first time the generation of pure amorphous silica from bamboo leaves, which was then used for preparing zeolite X solids loaded with different alkali metal cations (Na$^+$, K$^+$, Cs$^+$, and Ca$^{2+}$). The properties and the basicity of zeolite samples were characterised and their catalytic performances were further tested in the cyanoethylation reaction of various alcohols. The cyanoethylation reaction was performed under air atmosphere using instant heating that mimicked the microwave heating system.

Results and Discussion

Inorganic Content of Bamboo Leaf Ash

Thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) analysis were performed to follow the thermal decomposition pattern of the organic moieties and to determine the non-combustible inorganic content in the bamboo leaves. The thermogram of bamboo leaves showed 3 steps of weight loss (see Fig. S1, Supplementary Material). The first step of weight loss at $\leq$180°C (11.2%) originated from water desorption. The second step of weight loss at 160–380°C (46.8%) was due to the decomposition of hemicellulose and cellulose whereas the third step of weight loss at 380–600°C (10.3%) corresponded to the decomposition of lignin.[24] After the completion of TGA, 31.7% of solid remained as inorganic white ash, which was much higher than RHA (14–25%) and SCBA (10–25%).[20,25]

The elemental analysis of BLA was performed using X-ray fluorescence (XRF) spectroscopy. It was deduced that BLA had a SiO$_2$ content of 99.4% with only 0.26% of other inorganic elements detected (inset table in Fig. 1). Furthermore, the BLA produced was an amorphous solid according to the X-ray diffraction (XRD) analysis where only one broad hump was observed at 2$\theta$ = 28° in the diffractogram (Fig. 1).[26]

Zeolite X Solids

The XRD diffractograms of NaX, KX, CsX, and CaX are shown (Fig. 2). All zeolite X samples exhibited reflection peaks at 2$\theta$ = 6.2°, 10.0°, 11.7°, 15.4°, 18.4°, 20.1°, 23.4°, 26.7°, and 31.3°, which corresponded to the (111), (220), (311), (331), (511), and (642), and (555) planes of the FAU structure.[4] In addition, no miscellaneous diffraction peaks were observed in the XRD diffractograms indicating that no co-crystallisation of the LTA, SOD, and EMT phases occurred in the samples. Nevertheless, the diffraction peaks of KX, CsX, and CaX were slightly shifted compared with those of NaX. This should be due to the insertion of alkali metal cations with different sizes as extra framework cations in the FAU zeolite framework.[27]

The field emission scanning electron microscopy (FESEM) images of zeolite X solids were also captured. It can be seen that the morphology and size of zeolite X crystals were retained after ion exchange treatment (Fig. 3). All the crystals exhibited octahedron morphology and were sized 3.31 ± 1.21 μm. The extent of cation exchange, the unit cell compositions, cation electronegativity, surface area, and total pore volume of the zeolite X samples are tabulated in Table 1. All the ion exchanged zeolite X solids had a very high degree of ion exchange after 10 cycles of ion exchange, while the Si/Al ratio remained almost intact. In all cases, the full degree of the ion exchange could not

![Fig. 1. XRD pattern and elemental analysis of BLA.](image)

![Fig. 2. XRD patterns of (a) NaX, (b) KX, (c) CsX, and (d) CaX.](image)

![Fig. 3. SEM images of (a) NaX, (b) KX, (c) CsX, and (d) CaX.](image)
be achieved (CaX: 98 %, KX: 96 %, CsX: 85 %), which has also been reported previously. \cite{27,28} Divalent Ca\(^{2+}\) ions achieved the highest degree of ion exchange because one Ca\(^{2+}\) ion can compensate for two of the negative charges in zeolite X, which may accelerate the exchange rate of Na\(^{+}\) in the zeolite X framework. As a result, a slightly increased surface area and pore volume for the CaX zeolite were measured (Table 1). The elemental analysis of XRF was in line with the data obtained using inductively coupled plasma optical emission spectrometry (ICP-OES) analysis (Table S1, Supplementary Material).

The nitrogen adsorption-desorption isotherms of zeolites NaX, KX, CsX, and CaX are shown in Fig. 4. All the isotherms exhibited a type I adsorption pattern with high uptake in the P/P\(_0\), due to the presence of microporosity.\cite{30} In addition, the nitrogen uptake at low P/P\(_0\) is inversely proportional to the size of the exchanged cations. As a result, the CsX zeolite showed the lowest Brunauer–Emmett–Teller (BET) surface area (674 m\(^2\) g\(^{-1}\)) and pore volume (0.358 cm\(^3\) g\(^{-1}\)) (Table 1). In contrast, CaX zeolite exhibited the highest BET surface area (686 m\(^2\) g\(^{-1}\)) and pore volume (0.366 cm\(^3\) g\(^{-1}\)) because the zeolite framework is accommodated by the smaller divalent Ca\(^{2+}\). The nitrogen sorption results were in line with the XRF spectroscopy data, indicating that the porosity was slightly affected by the size and the charge of the metal cations.

Temperature-programmed desorption of carbon dioxide (CO\(_2\)-TPD) is one of the most famous methods for the characterisation of surface basicity. The study of the framework basicity is based on the bonding strength of CO\(_2\) with the basic sites of zeolite X (oxygen species).\cite{31} The CO\(_2\)-TPD plots of zeolite X samples are shown in Fig. 5. The TPD plot of NaX was composed of two peaks of CO\(_2\) desorption centred at 77.5\(^\circ\)C and 185.7\(^\circ\)C, which were attributed to the weak basic sites. The position of the CO\(_2\) desorption peaks progressively shifted towards higher temperature as the Na\(^{+}\) extra framework cations were ion exchanged with other cations. This indicated that the surface basicity of zeolite X framework gradually increased by decreasing the electronegativity of the extra framework cation, which resulted in the formation of strong and highly polar bonding of CO\(_2\)-zeolite X (Table 1).\cite{32} As interpreted, the basic strength of the solids followed the order of CsX > CaX ≥ KX > NaX.

**Catalytic Study**

**Effects of Extra Framework Cations and Reaction Time**

The catalytic performance of the zeolite X samples loaded with different types of alkali metal cations was tested on cyanoethylation between acrylonitrile and methanol in an Anton Paar’s instant heating reactor (Monowave-50) at 150\(^\circ\)C for 20 min. The acrylonitrile conversion against the reaction time and the rate constants for the reaction with NaX, KX, CaX, and CsX zeolite catalysts and without catalyst are shown in Fig. 6. As can be seen, a very low conversion (3.8 %) and small rate constant (2 \times 10^{-3} \text{min}^{-1}) were recorded when no zeolite catalyst was added into the reaction system. In contrast, the catalytic reaction took place with a much higher rate constant was obtained, producing 3-methoxypropanenitrile as the only product.
product when zeolite X solids were added. Among the zeolite samples studied, the highest rate constant (331 \times 10^{-3} \text{ min}^{-1}) was observed for zeolite CsX (Fig. 6B(e); Fig. S2, Supplementary Material). This catalyst with the highest basicity gave the highest conversion of acrylonitrile in the shortest time, i.e. 97% conversion was recorded after 11 min of reaction (Fig. 6A(e)). In contrast, CaX underwent cyanoethylation \sim 18 times slower than the CsX catalyst using the same reaction time and gave the lowest conversion (28.2%) among the four catalytic systems investigated (Figs 6A(b) and 6B(b)). The catalytic performance of zeolite X with different alkali cations could be observed in the order of CaX < NaX < KX < CsX, where the order generally followed the basic strength of the cations according to the CO\_2-TPD study. Zeolite CaX showed poorer catalytic performance than KX and NaX in this reaction because the divalent cation formed at the bottom of the quartz tube. As a result, the catalytic conversion was not able to be determined. Therefore, 150°C was considered as the optimal reaction temperature for this catalytic reaction system. The activation energy for this reaction over zeolite CsX was also calculated by using the Arrhenius equation and was found to be 29.21 kJ mol\(^{-1}\).

**Effect of Reaction Temperature**

Cyanoethylation was tested with methanol over the zeolite CsX catalyst at different temperatures (30, 50, 100, 120, 150, and 170°C) (Fig. 7). It was observed that the reactions performed at and below 50°C exhibited low conversion of acrylonitrile (<13.2%), which were due to an insufficient energy to activate the reaction. The conversion of acrylonitrile increased steeply with increasing temperature (>100°C), which could be attributed to the generation of gas pressure in the sealed quartz tube closed system; acrylonitrile and methanol have a boiling point of 77°C and 64.7°C, respectively. The highest acrylonitrile conversion (97.0%) was achieved at 150°C. Further increase of the temperature to 170°C, however, evidenced the degradation of chemicals where the reaction mixture turned black and a black solid was formed at the bottom of the quartz tube. As a result, the conversion percentage of acrylonitrile was not able to be determined. Therefore, 150°C was considered as the optimal reaction temperature for this catalytic reaction system. The activation energy for this reaction over zeolite CsX was also calculated by using the Arrhenius equation and was found to be 29.21 kJ mol\(^{-1}\).

**Effect of Molar Ratio of Reactants**

The effect of methanol to acrylonitrile molar ratio on the catalytic conversion was studied. The results showed that an increase in the methanol to acrylonitrile molar ratio from 0.5:1 to 6:1 led to a higher conversion of acrylonitrile from 42.3% to 98.0% (Fig. 8). The conversion, however, dropped slightly to 97.6% when the methanol to acrylonitrile molar ratio was further increased to 8:1. Hence, a methanol to acrylonitrile molar ratio of 6:1 was the optimal reaction feed for this catalytic reaction system.

**Effect of Type of Alcohol**

Cyanoethylation of various alcohols with acrylonitrile to form 3-alkoxypropanenitriles was carried out in the presence of zeolite CsX solid base catalyst at 150°C. Four aliphatic (methanol, ethanol, propanol, and butanol), one cyclic (cyclohexanol), and one aromatic (phenol) alcohols were chosen as the reaction substrates. The molecular weight, molecular size, and pK\(_a\) are tabulated in Table 2. Only the aliphatic alcohols were successfully converted to 3-alkoxypropanenitriles. The reaction using methanol gave the highest conversion (98.0%) due to high dissociation of CH\(_3\)O–H bonding (pK\(_a\) = 15.5) and its smallest molecular size that can easily diffuse into the supercages of CsX.

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**Fig. 6.** (A) Acrylonitrile conversion versus reaction time and (B) rate constants for the cyanoethylation reaction (a) without catalyst, and with basic zeolite catalysts of (b) CaX, (c) NaX, (d) KX, and (e) CsX. Reaction condition: acrylonitrile:methanol ratio = 1:4, \(T = 150^\circ\text{C}\).

**Fig. 7.** Effect of temperature on cyanoethylation reaction between acrylonitrile and methanol. Reaction condition: 0.10 g CaX catalyst, acrylonitrile: methanol ratio = 1:4, \(t = 11\) min.
zeolite. When the molecular size of linear chain alcohol became bulkier, the conversion rate decreased even though the pKₐ value increased. For instance, the reaction using butanol (5.95 × 1.87 × 3.21 Å³, pKₐ = 16.0) only recorded 9.3 % of the conversion because of its long carbon chain that disrupted its diffusion and accessibility to the basic sites, (Si–O–Al)⁻⁻Cs⁺, which were located in the supercages of zeolite X. However, no conversion was observed for the cyclic and aromatic alcohols. For phenol, which is the bulk and has low pKₐ, the electrons are easily stabilised by delocalization throughout the aromatic ring. Hence, the dissociation of PhO–H requires higher activation energy and thus leads to 0 % conversion. Similarly, no catalytic conversion was observed for cyclohexanol although it has a high pKₐ value. The reason is due to its bulkier molecular structure and the low tendency of activation of its O–H bond by zeolite active sites as a result of the steric hindrance effect. With the CsX zeolite solid base catalyst, the reactivity increased in the order of cyclohexanol = phenol < butanol (9.3 %) < propanol (12.7 %) < ethanol (32.1 %) < methanol (97.0 %). Hence, the order of the reactivity is explained by the molecular size of the alcohol besides the acid-base pairs, i.e. the acidity of the alcohol and the basic strength of the solid catalyst.

Catalyst Activity on Instant Heating, Microwave-Assisted and Reflux Reaction Environments

A comparative study on the effect of heating methods, namely non-microwave instant heating, microwave heating and normal reflux was attempted (Table 3). As shown, a low conversion (48.7 %) was observed under reflux conditions even after 12 h. In contrast, a high reaction conversion (99.8 %) and selectivity (100 %) were achieved by using microwave heating (Anton Paar Synthos 3000). The major advantage of using a microwave oven in organic synthesis is that it is fast and homogeneous heating can be achieved due to localised heating that enhances the product yield and selectivity. Interestingly, the results obtained using an instant heating synthesis reactor (Monowave 50) were comparable with those obtained using a microwave reactor. This suggested that the fast heat transfer and homogeneous heating created by microwave energy can be mimicked

**Table 2.** The catalytic conversion of acrylonitrile when reacted with different alcohols

<table>
<thead>
<tr>
<th>Alcohols</th>
<th>Molecular weight [g mol⁻¹]</th>
<th>pKₐ</th>
<th>Molecular size [Å³]¹</th>
<th>Conversion [%]²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>32.04</td>
<td>15.5</td>
<td>2.35 × 1.83 × 1.85</td>
<td>98.0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>46.06</td>
<td>15.9</td>
<td>3.69 × 1.79 × 2.00</td>
<td>32.1</td>
</tr>
<tr>
<td>Propanol</td>
<td>60.09</td>
<td>16.0</td>
<td>5.43 × 1.87 × 3.19</td>
<td>12.7</td>
</tr>
<tr>
<td>Butanol</td>
<td>74.12</td>
<td>16.1</td>
<td>5.95 × 1.87 × 3.21</td>
<td>9.3</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>100.15</td>
<td>16.0</td>
<td>5.07 × 4.33 × 2.82</td>
<td>0</td>
</tr>
<tr>
<td>Phenol</td>
<td>94.11</td>
<td>10.0</td>
<td>5.78 × 4.27 × 0.99</td>
<td>0</td>
</tr>
</tbody>
</table>

¹Ref. [36].
²The molecular size was estimated using HyperChem 7.0 software.
³Reaction condition: 0.10 g CsX catalyst, alcohol : acrylonitrile ratio = 6 : 1, T = 150°C, and t = 11 min.

**Table 3.** Comparative catalytic study under different heating environments

<table>
<thead>
<tr>
<th>Heating method</th>
<th>Conversion [%]</th>
<th>Selectivity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-microwave instant heating (Monowave 50)⁴</td>
<td>98.0</td>
<td>100</td>
</tr>
<tr>
<td>Microwave heating (Synthos 3000)⁵</td>
<td>99.8</td>
<td>100</td>
</tr>
<tr>
<td>Normal reflux</td>
<td>48.7</td>
<td>100</td>
</tr>
</tbody>
</table>

⁴Reaction condition: 0.10 g CsX catalyst, alcohol : acrylonitrile ratio = 6 : 1, T = 150°C, and t = 11 min.
⁵Reaction condition: 0.10 g CsX catalyst, alcohol : acrylonitrile ratio = 6 : 1, T = 150°C, and t = 12 h. The condenser was tightly sealed and under cool water circulation (4°C) to prevent evaporation.
by using strong stirring and instant heating. Similar observations have also been reported by Obermayer et al.\cite{23} and Bana et al.\cite{36,37}

Catalyst Reusability

The reusability of solid catalysts is a major challenge for industrial applications.\cite{38} In this study, zeolite CsX catalyst was recovered after each cycle of reaction, washed with diethyl ether, and activated before use for the subsequent reaction cycles. It was shown that the product selectivity remained constant and the conversion percentage did not decrease significantly after 5 consecutive reaction cycles (Fig. 9). The conversion rate was maintained up to 96.7% even after the fifth cycle of reaction. In addition, the XRD pattern of the recovered zeolite CsX was also recorded (Fig. S3, Supplementary Material). It was found that the XRD pattern was almost similar to that of the fresh CsX zeolite. Thus, the results explained that the zeolite structure remained intact after the catalytic reaction and the Cs\(^+\) extra framework cations were still electrostatically bounded to the surface of the zeolite. As a result, the zeolite remained catalytically active to the cyanoethylation reaction with negligible leaching and deactivation (coking) problems. In this case, the high reusability of zeolite CsX synthesised from BLA allows it to be used as an excellent solid base catalyst in industrial catalytic applications.

Conclusion

In conclusion, a high content of silica ash can be obtained from bamboo leaf agriculture waste. The BLA was found to be completely amorphous and was successfully used as the silica source for preparing zeolite X with various alkali metal cations (Na\(^+\), K\(^+\), Ca\(^{2+}\), and Cs\(^+\)). The prepared zeolite solids exhibited high crystallinity and high porosity according to XRD, SEM, and nitrogen adsorption studies. Additionally, the basic strength of the zeolite catalysts was investigated using pyrrole adsorption. The microporous solids were applied in catalytic cyanoethylation of the methanol reaction using an instant heating synthesis reactor. The catalytic performance of zeolite X with different alkali cations was significantly enhanced under the aforementioned condition and could be observed in the order of CsX < NaX < KX < CaX, where the order followed the basic strength of the cations based on the pyrrole adsorption study. Furthermore, various reaction parameters had also been studied.

The optimal conditions for cyanoethylation of methanol reaction were documented to be: 0.10 g CsX catalyst, alcohol : acrylonitrile ratio = 6 : 1, reaction temperature = 150°C, and reaction time = 11 min. In addition, the catalytic performance under the instant heating condition not only was comparable to the microwave synthesis system but also was superior than under the normal reflux conditions. We propose that our current work would be helpful in providing insights on the advantage of the instant heating process for further study under the non-microwave instant heating condition for other chemical reactions.

Experimental

Preparation of BLA

Bamboo leaves obtained from a local bamboo factory were first washed thoroughly with water to remove the dirt. The leaves were then air-dried before being cut into small pieces (∼3 cm × 3 cm). The leaves were treated with nitric acid (1.5 M, 1 L, QRe©) under agitation (90 rpm, 15 h). Next, the leaves were washed with distilled water until the pH was 7. The leaves were air-dried before being blended into fine pieces. The leaves were combusted at 600°C for 5 h with a heating rate of 1.0°C min\(^{-1}\). Pure white ash (31.7% by mass) was collected after the combustion process. The BLA preparation flow procedures are summarised in Fig. 10.

Synthesis of Zeolite NaX

The zeolite NaX was synthesised by using our newly developed recipe. NaOH (12.000 g, Merck, 99%) and BLA (5.000 g) were first introduced into a polypropylene bottle. Distilled water (145.338 g) was added and the mixture was magnetically stirred (3.178 g, Sigma-Aldrich, 53% Al\(_2\)O\(_3\), 42.5% Na\(_2\)O) and NaOH (0.588 g, Merck, 99%) in distilled water (151.270 g). The aluminate solution was then added slowly to the silicate solution under stirring (500 rpm). The resulting gel mixture with a molar composition of 5SiO\(_2\) : 1Al\(_2\)O\(_3\) : 2Na\(_2\)O : 100H\(_2\)O was further stirred for an additional 10 min before subjecting to hydrothermal treatment (90°C, 9 h). After crystallisation, the solid product was recovered by centrifugation (3100 g, 10 min) and washed by distilled water. This step was repeated until the supernatant was pH 7. The solid obtained was dried at 90°C overnight and labelled as zeolite sample NaX.

Preparation of LiX, KX, CsX, and CaX Zeolites

The ion-exchange process was carried out as follows: Dried NaX powder (1.500 g) was stirred with LiCl, KCl, CsCl, and NaCl solutions. The resulting gel mixture with a molar composition of

![Fig. 9. Reusability test of zeolite CsX in cyanoethylation reaction between acrylonitrile and methanol.](Image)

![Fig. 10. Procedures of preparation of bamboo leaf ash (BLA).](Image)
CaCl₂ solutions (100 mL, 0.50 M), respectively, at 60°C for 6 h. The solid samples were separated from the liquid phase by centrifugation (3100 g, 10 min). The ion exchange process was repeated for 10 times to ensure that the highest degree of ion exchange was achieved for each alkali metal cation. The samples were then washed with distilled water (100 mL) for 5 times, followed by drying in an oven at 90°C overnight. The degree of ion exchange was calculated using Eqn 1:

$$\text{Ion exchange(%) = } \frac{[\text{Na}]_{\text{BIE}} - [\text{Na}]_{\text{AL}}}{[\text{Na}]_{\text{BIE}}} \times 100\%$$

(1)

where [Na]_{BIE} and [Na]_{AL} are the concentrations of sodium in zeolites before and after ion exchange, respectively.

Characterisation

TGA on the bamboo leaves was performed using a Mettler TGA SDTA851 instrument with a heating rate of 10°C min⁻¹ under constant air flow (100 mL min⁻¹). The XRD patterns of the samples were recorded by a Siemens D5000 Kristalloflex diffractometer (CuKα radiation, 3–45°, step size 0.01°, 2.0 s per step). The morphology of the zeolite samples was studied by a Nova NanoSEM™ field emission scanning electron microscope with an accelerating voltage of 20 kV. The chemical composition of the solids was determined using Phillips X’Unique XRF and Optima 8300 ICP-OES spectrometers. The porosity analysis was performed using a Micromeritics ASAP 2010 instrument. The powder (~50 mg) was first dehydrated at 300°C under vacuum overnight before the measurement at ~196°C. The basicity of zeolite samples was characterised by a CO₂-TPD analyzer (AutoChem II 2920). The samples were first degassed at 500°C to remove any adsorbed species on the catalytic surface. CO₂ was then introduced and adsorbed onto the samples. The investigated samples were heated up to 900°C at 10°C min⁻¹ to observe the distribution of CO₂ adsorbed on the surface of samples. The amount of desorbed CO₂ was then monitored quantitatively by a thermal conductivity detector (TCD).

Catalytic Testing

Prior to the catalytic testing, the water content in 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 Haën) and Hydranal solvent CM (Riedel-de Haén). Both reagents were analysed twice to obtain the average values by direct injection without preliminary treatment.

Then, methanol (76 mmol), acrylonitrile (19 mmol), activated zeolite X samples (0.100 g, pre-heated at 400°C for 3 h), and a small magnetic stirring bar were transferred into a quartz reaction tube, capped, and inserted into an instant heating synthesis reactor (Anton Paar Monowave). The high pressure quartz glass tube was magnetically stirred (300 rpm) and heated to the desired temperature (30–170°C) using a fast heating mode; it took less than 2 min to reach the desired temperature. Then, a 1 to 20 min hold time was set to allow the reaction to take place. After completion of the reaction, the solid catalyst was recovered from the reaction mixture by centrifugation (3100 g, 10 min). The reaction mixture was analysed using a gas chromatograph (GC Hewlett-Packard 5880) equipped with an HP-5 non-polar capillary column. The catalytic testing was repeated for 3 times. The average conversion and its standard deviation were then determined.

The reusability test of zeolite catalyst was carried out as follows: The spent catalysts after the reaction were first washed with diethyl ether and acetone. The washed catalyst was then air-dried and activated again (400°C, 3 h) before being used for the subsequent cycles of the reaction. The reaction mixture was separated from the solid catalyst and analysed using GC.

Supplementary Material

TG and DTG plots of bamboo leaves, GC chromatographs of the catalytic reaction, XRD patterns before and after the reaction cycles, and ICP-OES data of the zeolite samples are available on the Journal’s website.

Conflicts of Interest

The authors declare no conflicts of interest.

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References