

Synthesis of Zeolites from Sugarcane Bagasse Ash in The Presence of Cationic Surfactants

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Abstract: Bagasse ash contains relatively high silica and can be used as a source of silica in zeolite synthesis. The presence of cationic surfactant CTA⁺ can increase the crystallinity of zeolite. This research examines the effect of CTA⁺ surfactant concentration on zeolite crystallinity. The synthesis method is hydrothermal with a temperature of 150 °C for seven days. The calcination temperature to decompose CTA⁺ surfactant is 650 °C. The results showed samples without CTA⁺ were a mixture of Hydrogen Aluminum Silicate (HAS), Aluminum Silicate Hydroxide, and Kaolite. In contrast, samples with CTA⁺ surfactants produced a variety of Aluminum Silicate Hydroxide, kaolite, and Donbassite. From this study, it can be concluded that the greater the concentration of surfactants, the greater the crystallinity of the product and the emergence of new minerals, namely donbassite.

Keywords—bagasse ash; zeolites; surfactant; CTA⁺; crystallinity

1. INTRODUCTION

Sugarcane processing produces granulated sugar as the main product and makes residual material with no economic value, which is referred to as waste. One of the sugar factory's solid wastes is bagasse, which is used as fuel for cooking sap or as a mixed pulp for making paper. Using abundant natural resources as alternative raw materials has been studied intensively because it is more economical and can reduce solid waste. Many researchers have carried out zeolite synthesis using biomass waste as a source of Si and Al [1]. Sugarcane bagasse ash contains silica, alumina, and other materials that can be used to become more valuable materials. The silica content successfully extracted from sugarcane bagasse through extraction and precipitation using HCl was 70.85% [2]. In contrast, we obtained 98.4% if extracted using the alkaline method at low temperatures and acid deposition [3]. Several researchers have succeeded in synthesizing zeolite from bagasse ash, such as zeolite A [4], [5], and NaP1 [6].

Zeolites are aluminosilicate crystals with a three-dimensional structure. Zeolites are formed by condensation polymerization of tetrahedral silicates and aluminates. The zeolite structure is negatively charged so that there are balance cations that can be exchanged [7]. In addition, zeolites have a unique pore size and shape structure. Zeolite pores can be adjusted in such a way using surfactants. The balancing cations are exchanged with cationic surfactants such as cetyltrimethylammonium (CTA). Various studies have used CTA surfactants as a structural directing [8], [9] or to produce good porosity [10] and crystallinity [11].

Surfactant concentration is one of the crucial factors that can affect the synthesized product material. The higher the concentration of surfactants, the saturation of the solution increases, and the concentration of monomers also increases. Thus, the concentration of micelles also increases. When CMC is reached, a constant monomer concentration can

trigger the formation of new micelles to form an orderly arrangement of the material frameworks [12].

2. METHODOLOGY

2.1 Materials

Sugarcane bagasse waste, Sodium hydroxide pellets (Merck), demineralized water, Hydrochloric acid 37% (Merck), Aluminium hydroxide powder (Merck), cetyltrimethylammonium bromide powder (Merck).

2.2 Equipment and Instrumentations

Glassware, porcelain cup, Teflon container, magnetic stirrer rod, Whatman 42 filter paper, hot plate, analytical balance (Ohaus), oven, X-Ray Diffractometer (X-RD), Fourier Transform Infrared Spectroscopy (FTIR).

2.3 Procedures

2.3.1 Sugarcane bagasse ash preparation

The sugarcane bagasse waste is cleaned and burned to obtain charcoal. Furthermore, the ash processing is carried out in a furnace at a temperature of 650 °C for 4 hours. The resulting ash was ground and sieved to a size of 100 mesh. The Si and Al content were analyzed using Atomic Adsorption Spectroscopy (AAS).

2.3.2 Zeolite synthesis process

A total of 10 grams of bagasse ash was soaked in a 2 M NaOH solution for 24 hours. The mixture is separated, and the filtrate is a sodium silicate solution. A total of 11.2 g NaOH was added to distilled water until the volume was 100 mL. The solution was heated, and 2.04 g Al(OH)₃ was added to the solution to obtain a sodium aluminate solution. Sodium silicate solution was reacted with sodium aluminate (ratio of SiO₂/Al₂O₃ = 50), stirred and heated at 80 °C for 20 minutes. Then the CTA surfactant solution (concentration variation of 0.05 M; 0.1 M; 0.15 M; and 0.2 M) was added to the mixture.

Furthermore, the mixture was stirred and heated at 60°C for 30 minutes. The remedy was conditioned to have a pH = 11 with the addition of 0.1 M HCl. After that, it was heated at 150°C in an oven for 7 days. The product formed was filtered and washed with distilled water until pH=7. After that, the product was dried at 105°C for 10 hours and then calcined at 600°C for 5 hours to remove the surfactant. The final result in the form of white solids was analyzed using FTIR and XRD.

3. RESULTS AND DISCUSSIONS

3.1 Sugarcane Bagasse Ash

The burning of bagasse aims to turn the dregs into charcoal. The charcoal is heated/calcined in the furnace at a temperature of 650 °C for 4 hours until brownish-white ash is obtained. The purpose of the calcination process is to remove organic compounds in bagasse because it is decomposed into CO₂ and H₂O gas. At the same time, the components of inorganic compounds are converted to oxides. In this case, it is more focused on SiO₂ and Al₂O₃. The results of the AAS analysis showed that bagasse ash contained 30.45% Si and 3.11% Al.

3.2 Zeolite product

Using CTA surfactant in zeolite synthesis aims to form and homogenize the pores of the synthesized zeolite to obtain a product with a regular framework. All mixtures were stirred and heated at 80°C for 30 minutes to form a zeolite polymer through condensation polymerization. Ageing is done to improve the formation of zeolite polymers. During the ageing process, sodium silicate with H₂O reacts to form monomers free of silicic acid.

The system is conditioned at a pH = 11 using HCl. This acidity condition is related to the presence of Si₄O₈(OH)⁴⁻ species and Al(OH)₄⁻ [13]. These species interact to form a silica-alumina polymer which will affect the rate of nucleation and crystal growth [14]. The solution will also be found in species different at different levels of basicity. An acidic solution with a pH of 1–4 aluminium cations octahedral [Al(H₂O)₆]³⁺ dominant. In the pH range of 2–6, oxy-aluminium cations were also found. The aluminate species associated with polymer formation silica-alumina is Al(OH)₄⁻, and the maximum concentration can be found at pH ≥ 9. The optimum concentration of Si⁴⁺ species is at pH 11 or 12, so the synthesis was carried out on the expected optimum reaction in this study.

The Addition of cationic surfactant CTA⁺ serves as a structural directing or pore-forming template. Templates function like cations to neutralize the negative on the zeolite framework. In the mixture, cation CTA⁺ will react quickly with the anionic monomers silicate and aluminate assembling the structure to form a zeolite crystal embryo.

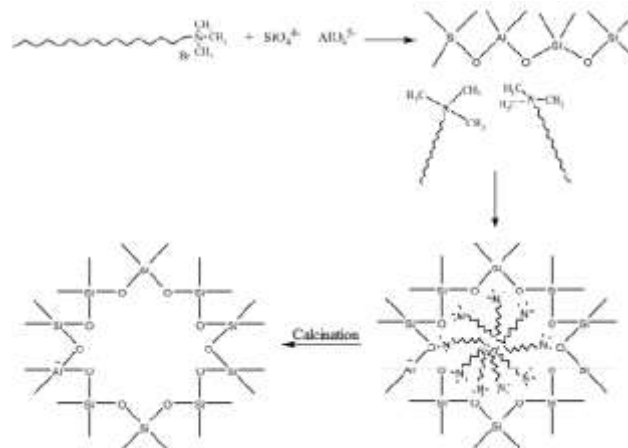


Fig. 1 Schematic of forming zeolite in the presence of cationic surfactant

Figure 1 shows that aluminate and silicate ions interact with surfactants when in solution. The interaction occurs through electrostatic bonds. The CTA⁺ surfactants form micelles to reduce surface tension, the hydrophobic groups will gather, and the hydrophilic heads of the surfactants will move away from each other to form a cylindrical circle. The hydrophilic group will interact with the primary building unit (primary building unit) of TO₄ by electrostatic interaction. The primary structural unit of zeolite is a tetrahedral consisting of a central Si or Al atom surrounded by four oxygen atoms, namely [SiO₄]⁴⁻ or [AlO₄]⁵⁻ [15].

Hydrothermal crystallization process at a temperature of 150 °C for 168 hours. At the stage of crystal formation, the amorphous gel will undergo a rearrangement in its structure by heating so that a crystal nucleus embryo can be formed. In this state, there is an equilibrium between the crystalline core embryo, the remaining amorphous gel, and the supersaturated solution. The process is in a metastable state. If the residual amorphous gel dissolves again, crystal growth will occur from the core embryo until the remaining amorphous gel is used up and crystals are formed in a stable state. This stage is the stage of crystal growth [16].

The calcination aims to decompose surfactants which are both structural guides and templates. Calcination was carried out at a temperature of 650°C, where the thermal decomposition temperature of the CTA⁺ surfactant was only 250°C. At this temperature, it is expected to be able to decompose CTA⁺ so that it leaves open pores completely.

3.3 Product Characters

The X-Ray Diffraction (X-RD) method is a qualitative analysis method that provides information about the crystallization of a material and can be used to identify the composition of the material. This is because each mineral has a characteristic diffractogram pattern. The crystallinity of the sample is seen from the appearance of the diffractogram pattern. A diffractogram with a clear, high, sharp split pattern of peaks has good crystallinity.

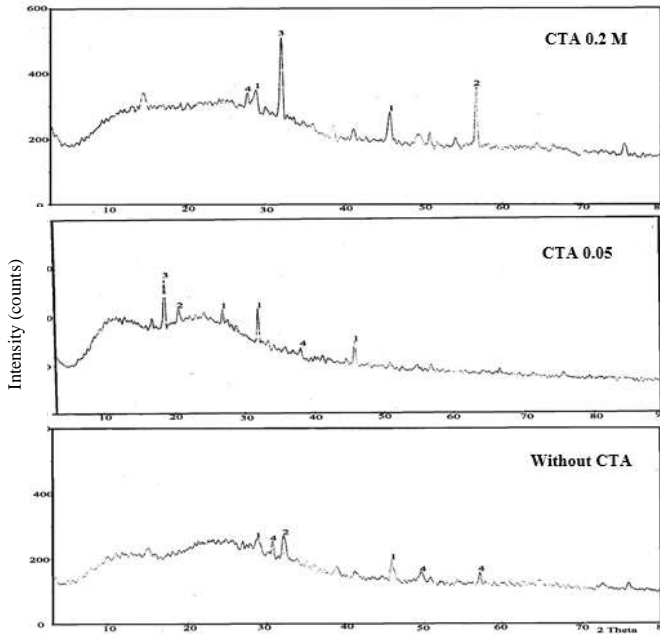


Fig. 2 The XRD of synthesized zeolite without and with a CTA⁺ cationic surfactant

Figure 2 shows that the more surfactants are added, the crystallinity of the product also increases. This is because the more concentration of CTA⁺ added will increase the saturation level of the solution so that more crystals are formed. But in this study, the product was not optimal. This is because not all silica can be extracted during the extraction process, so the zeolite polymerization formation process does not optimally.

TABLE I. THE RELATIVE COMPOSITION OF MINERALS IN EACH SYNTHESIS PRODUCT

Samples	2θ	2θ JCPDS standart	Intensity	Minerals
Without CTA	32.23	32.51	49	Kaolite
	45.82	45.40	45	
	30.78	30.08	34	
CTA 0.05 M	18.61	18.82	129	Donbassite
	31.98	31.91	98	
	20.66	20.14	40	
	37.98	37.80	30	
CTA 0.2 M	31.88	31.91	171	Donbassite
	56.64	56.52	138	
	45.65	45.40	67	
	27.63	27.45	38	

Description of abbreviations: HAS: hydrogen Aluminium silicate, ASH: aluminum silicate hydroxide

Table 1 shows that the mineral intensity in each sample is not the same, possibly due to the different X-rays being absorbed in each sample. In the synthesized material with the addition of surfactants, a new mineral has emerged, namely donbassite. Each mineral has different formation conditions, so it is possible that the addition of surfactants can support the nucleation process in the donbassite mineral.

The FTIR analysis aims to determine the groups formed in the resulting material and the presence of a guide molecule that may still be left behind. The FTIR spectra of the synthesis are shown in Figure 3. Figure 3 shows the FTIR spectra of the synthesis with various concentrations of CTA⁺ surfactants, namely 0.15 M, 0.6 M and without CTA⁺.

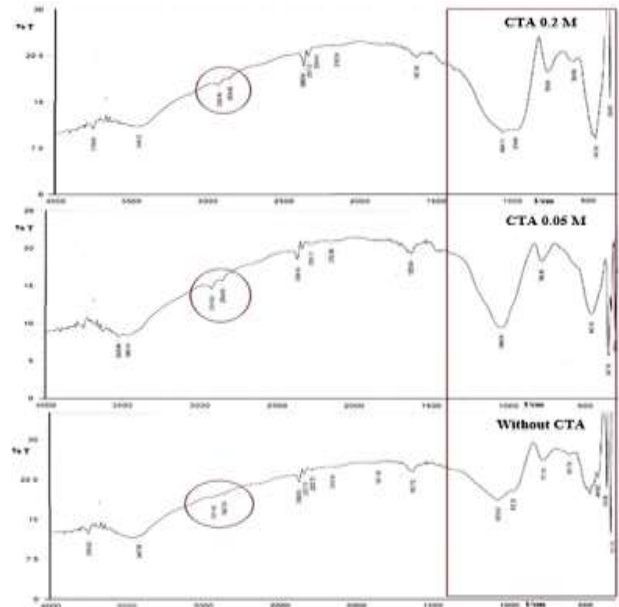


Fig. 3 The FTIR spectra of synthesized zeolite without and with a CTA⁺ cationic surfactant

In the zeolite structure, there are internal and external bonds. The internal bond of the synthesized zeolite appears at wave numbers around 1250-950 cm⁻¹, indicating the presence of asymmetric stretching vibrations of Si—O and Al—O of the aluminosilicate framework. All synthesized zeolites showed absorption in this area. The Si-O and Al—O symmetric stretching vibrations appear in the absorption region around 820-650 cm⁻¹, which is indicated by the appearance of absorption peaks in all samples.

Double ring is a specific zeolite character indicated by the appearance of absorption in the area of 650–500 cm⁻¹. This double ring is an external braid between the zeolite layers with each other. The absorption in this area was shown by two synthesized zeolites, namely at 0.6 M CTA⁺ and without CTA⁺, although the absorption was deficient, while the synthesized zeolite with 0.15 M CTA⁺ did not appear. This is because the heating process is not wholly. The bending vibrations of Si-O and Al-O in the aluminosilicate framework of the zeolite appear in the absorption region of about 500-420 cm⁻¹. The stretching and bending vibrations of Si-O and Al-O indicate that an aluminosilicate framework has been formed in each sample.

Figure 3 also indicates that the synthesis product that has been calcined at a temperature of 650 °C no longer contains CTA surfactants. In other words, CTA⁺ has decomposed. In the spectra, no absorption was found at wave number 2950-

2850 cm^{-1} , which is a typical stretching vibration for the C-H group of CTA^+ .

4 CONCLUSIONS

Based on the results and discussion, it can be concluded that the synthetic product without using CTA^+ consists of a mixture of hydrogen aluminium silicate (HAS), aluminium silicate hydroxide (ASH) and kaolinite. The synthesis product using the cationic surfactant CTA^+ contains a mineral mixture of Aluminium Silicate Hydroxide, kaolinite, and donbassite. The presence of cationic surfactant CTA^+ improves the crystallinity of the synthesis product.

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