Synthesis of silicalite-1 zeolite using silica from elephant grass (Pennisetum purpureum)

C D D Sundari1,*, S Setiadj2, A Andriani3, E Sumiyanto3 and A L Ivansyah3,4

1 Department of Chemistry Education, UIN Sunan Gunung Djati Bandung, Jl. Cimincrang, Cimenerang, Panyileukan, Bandung, West Java, 40292, Indonesia
2 Department of Chemistry, Faculty of Science and Technology, UIN Sunan Gunung Djati Bandung, Jl. A.H. Nasution No.105 Bandung, West Java, 40614, Indonesia
3 Master Program in Computational Science, Faculty of Mathematic and Natural Science, Institut Teknologi Bandung, Jl. Ganesha No. 10, Bandung, West Java, 40132, Indonesia
4 Analytical Chemistry Research Group, Department of Chemistry, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Jalan Ganesha No. 10, Bandung, Indonesia

*citrac@uinsgd.ac.id

Abstract. Silicalite-1 is a type of zeolite with no aluminum content and is hydrophobic. This zeolite can be synthesized from various types of silica. Elephant grass (Pennisetum purpureum) is one of the potential agricultural wastes that has a fairly high silica content that can be used for zeolite synthesis. In this study, silicalite-1 zeolite was synthesized using silica extracted from elephant grass and tetrapropylammonium bromide (TPABr) templates. Silica samples extracted from elephant grass have 71.91% amorphous SiO2 content. Silicalite-1 zeolite was synthesized with molar ratio of 1SiO2 : 0.527TPABr : 0.395Na2O : 98.45 H2O, using hyrothermal method at 180°C for 24 hours in a stainless steel-teflon lined autoclave. The resulting silicalite-1 samples were confirmed by X-Ray Diffraction (XRD) and showed 2θ which was typical for silicalite-1 i.e. 8.02°, 8.93°, 23.09°, and 23.98°. The results of Scanning Electron Microscopy (SEM) show that silicalite-1 zeolite has hexagonal crystals with 43.36 µm size as a result of the calculation using the Scherrer method.

1. Introduction

Zeolite is an aluminosilicate hydrate mineral composed of tetrahedral-tetrahedral alumina (AlO₄⁻) and silica (SiO₄⁴⁻) which form a negatively charged structure and open / porous hollow. Zeolites are widely used as cation exchangers, water softening, molecular sieves, drying agents, adsorbents, and as catalysts or catalyst carriers for various chemical reactions [1]. Zeolite based on its source can be divided into two, namely natural zeolite and synthetic zeolite. Natural zeolite usually contains cations of K⁺, Na⁺, Ca²⁺, and Mg²⁺ [1]. While synthetic zeolites usually only contain K⁺ and Na⁺ cations. One type of synthetic zeolite is zeolite silicalite-1 [1].

Zeolite synthesis in general must use silica sources, aluminum sources, templates, and hydrothermal synthesis [2]. The source of silica commonly used for zeolite synthesis is TEOS (Tetraethyl Orthosilicate) [3], Silica LUDOX [4], Na₂SiO₃ [5] which are relatively expensive silica sources. Thus,
an alternative silica source is needed to replace commercial silica sources with silica sources that are relatively inexpensive. One of the relatively inexpensive silica sources for zeolite synthesis is silica which is isolated from agricultural waste, such as rice husk waste [6,7], bamboo leaf [8,9], and elephant grass [10]. Rusdiyana has reported that in elephant grass contains a lot of lignin and silica [11]. Silica isolated from elephant grass was used as precursor for ZSM-11 zeolite synthesis [10], but has not been used for silicalite-1 synthesis.

In this study, silica was isolated from elephant grass using the sol-gel method and synthesis of silicalite-1 zeolite was carried out using the isolated silica as silica source by hydrothermal method. It is hoped that this study can increase the economic value of elephant grass and also increase performance-cost ratio for silicalite-1 synthesis.

2. Methodology

2.1. Silica isolation

Elephant grass was washed thoroughly with water, then dried in an oven at 105 °C for 5 hours, burned, and then calcined at 550 °C for 5 hours. The resulting ash was put into Erlenmeyer and added 1 M NaOH. The mixture was stirred accompanied by heating at 150 °C for 1 hour. The mixture was filtered in hot conditions using a Buchner filter to obtain a colorless filtrate. H2SO4 3M was added dropwise to the filtrate until pH 7. The white gel formed was left to stand for 24 hours, then filtered, washed with hot aqua DM and then dried at 80 °C for 24 hours. The dried solids were analyzed using EDX, XRF, XRD, and FTIR.

2.2. Silicalite-1 synthesis

The isolated silica was weighed and mixed into a mixture consisting of 1 M NaOH solution, TPABr and H2O with molar ratio of 1SiO2: 0.527 TPABr: 0.395 Na2O: 98.45 H2O. The mixture was stirred using a magnetic stirrer for 24 hours in a polypropylene bottle, then the mixture was put into a teflon lined stainless-steel autoclave. The autoclave is heated in an oven at 180 °C for 24 hours. The autoclave was cooled to room temperature, then the solution was filtered. The resulting solid was washed using aqua DM, then dried in an oven at 110 °C for 24 hours and calcined at 500 °C. The resulting silicalite-1 was analyzed using XRD, SEM, and FTIR.

3. Results and discussions

3.1. Isolation of silica from elephant grass

In silica isolation step, heating was done to accelerate the dissolution of silica in NaOH to form Na2SiO3 [12]. Silica, in the form of sodium silicate solution, was then reacted with a solution of H2SO4 3M as precipitation agent. Sulfuric acid solution is used to re-convert dissolved sodium silicate into SiO2. Water content in the product can be removed by drying in the oven [13].

EDX analysis of the isolated silica was carried out to determine the content of SiO2. From the results of EDX analysis, the percentage of SiO2 in the isolated silica was 71.91%. The results of EDX analysis can be seen in Table 1.

Table 1. EDX analysis of elephant grass’ silica.

| Oxide | Quantity (%) | Element | Quantity (%) |
|-------|--------------|---------|--------------|
| C     | 0,78         | C       | 0,78         |
| O     | 42,41        | Na      | 2,00         |
| Na2O  | 2,69         | Mg      | 0,36         |
| SiO2  | 71,91        | Si      | 33,61        |
| K2O   | 4,31         | K       | 3,58         |
The SiO$_2$ content of the isolated silica from elephant grass is quite large even though the percentage of its content is still below the content of silica from rice husk which is commonly used as a source of silica for the synthesis of zeolite. Silica content in rice husks reaches 85-98% [14]. Whereas when compared with silica from corn cobs which have also been widely isolated, the percentage of silica from elephant grass is greater than silica from corn cobs where the percentage of silica from corn cobs is equal to 50.36% [15]. Based on the data above, silica from elephant grass with a high percentage of SiO$_2$ content can be used as an alternative to silica from rice husk for substitute for commercial silica such as TEOS and LUDOX for the synthesis of zeolite.

XRF analysis was carried out to strengthen the EDX analysis. XRF analysis was carried out using two methods, i.e. soil method and alloy method. The results of XRF analysis using soil method can be seen in Table 2, while the results of XRF analysis using alloy method can be seen in Table 3.

**Table 2.** XRF analysis (soil method) of elephant grass’ silica (L.E. : Light Element).

| No | Element | Concentration (ppm) |
|----|---------|---------------------|
| 1  | K       | 5800 ± 1000         |
| 2  | Cl      | 4000 ± 3000         |
| 3  | Ni      | 42 ± 8              |
| 4  | Fe      | 35 ± 8              |
| 5  | Rb      | 26 ± 14             |
| 6  | Cd      | 22 ± 19             |
| 7  | Ag      | 21 ± 17             |
| 8  | Zn      | 21 ± 3              |
| 9  | Sr      | 5 ± 4               |
| 10 | Zr      | 2 ± 5               |
| 11 | Cu      | 2 ± 5               |
| 12 | Br      | 1 ± 3               |
| 13 | L.E.    | 990400 ± 1400       |

L.E. (Light Element) is an element with an atomic number (Z) of less than 18. The soil method is done to detect elements in the sample, but in this method, light element (L.E) is very small to be detected so that the alloy method is used as a support for detecting elements on the sample. However, from the results of the analysis the Si content is so high that no other elements or other elements are detected in very small amounts so that Si is considered 100%.

**Table 3.** XRF analysis of elephant grass’ silica using alloy methods.

| No | Element | Concentration (%) |
|----|---------|-------------------|
| 1  | Si      | 100               |
|    | Total   | 100               |

X-ray diffractogram of the isolated silica can be seen in Figure 1. The widepeaks show that the isolated silica from elephant grass has amorphous phase. The amorphous phase has more reactive properties compared to the crystalline phase, because the amorphous phase has irregular SiO$_4$ tetrahedral arrangement [16]. Amorphous reactive properties are caused by the presence of silanol groups and siloxane groups on the surface of silica gel.
In the results of the isolated silica FTIR spectrum (Figure 2) there is an asymmetric stretching vibration of the Si-O group in the siloxane (Si-O-Si) group in the wave number regions 811, 956, and 1284.35 cm\(^{-1}\). Peak at wave number 2352.73 cm\(^{-1}\) which is Si-O siloxan buckling vibration [12] and at wave number 3637.08 cm\(^{-1}\) shows the presence of hydroxy (-OH) vibration on silanol (Si-OH) groups. The presence of peaks at wave number 811, and 956 cm\(^{-1}\) has confirmed the formation of silica because it is related to the ring structure of SiO\(_4\) tetrahedral.

3.2. Synthesis of silicalite-1 zeolite

The synthesis of silicalite-1 zeolite does not involve Al, because silicalite-1 zeolite itself is a zeolite which has high Si content with zero Al content. TPABr is used as a template that contributes to the formation of zeolite pores during zeolitization. Alkalinity is an important medium in zeolite synthesis because pH affects the saturation of solutions and crystallinity. Increasing the concentration of OH\(-\) ions will lead to faster crystal growth. A high pH will produce a saturated solution of silicate [13]. Zeolite synthesis was carried out at 180 °C for 24 hours, because during the synthesis process silicalite-1 zeolite requires a higher temperature for the crystallization process. Temperature can affect rate of crystal growth.

The diffractogram of silicalite-1 zeoliteshowed a similar pattern with the standard ZSM-5 diffractogram shown in Figure 3. The XRD pattern of zeolite silicalite-1 formed peaks at 2\(\theta\) 8.02°, 8.93°, 23.09°, and 23.98°. The peaks in this area show similarities to the standard ZSM-5 diffractogram, i.e. at 2\(\theta\) 7-9°, 23.05°, and 23.8°. Diffractogram shows sharp peaks that shows the crystallinity of the synthesized silicalite-1 zeolite is quite high and shows that there is no other crystalline phase in the synthesis of silicalite-1 zeolite [17].

The FTIR spectra of silicalite-1 spectrum are shown in Figure 4. The absorption area around 1100-700 cm\(^{-1}\) is a zeolite fingerprint where there is a vibration of Si-O and Al-O. In this spectra the Si-O vibration is present at wavenumber 1003.95 cm\(^{-1}\), and does not indicate a vibration of Al-O. Whereas at wave number 1250-950 cm\(^{-1}\) shows the existence of internal bond on zeolite, in the form of stretching Si-O asymmetric. The spectra at wavenumber 820-650 cm\(^{-1}\) indicate the presence of stretching Si-O symmetry. The important characteristic of zeolite is the double ring. Double ring can be seen at wave number 650-500 cm\(^{-1}\) which indicates an external bond between zeolite. In the ZSM-5 zeolite, the external bond is the pentacyl. Peak at the number 558.86 cm\(^{-1}\) which indicates the presence of a pentacyl group which is the framework of the composition of the MFI type zeolite and the bending vibration of Si-O in the zeolite framework appears at the wave number 500-420 cm\(^{-1}\)
Figure 3. Diffractogram of synthesized silicalite-1 zeolite compared with ZSM-5 zeolite.

Figure 4. FTIR spectra of the synthesized silicalite-1.

There is a significant difference between the silica FTIR spectrum and the spectrum of silicalite-1 zeolite, this occurs because of vibrational shifts and phase differences. The phase of silica is amorphous so it produces peaks that are not sharp, whereas for zeolite silicalite-1 has a crystalline phase which causes the spectrum to have sharp peaks, due to differences in bond strength and vibration strength which for the crystalline phase has bond strength and strength more uniform vibration compared to silica which has an amorphous phase.

Based on the data from SEM analysis, the silicalite-1 zeolite shown in Figure 5 shows results that are not much different when compared with the results of the Fereydoon et al. [18] who used LUDOX as a source of silica and TPABr as a template.Crystals have a hexagonal shape that is characteristic of the MFI type zeolite [18]. The crystal size is around 40 μm. The synthesized silicalite-1 zeolite has a smaller crystal size than previous studies, thus has a greater surface area [18]. SEM results is in accordance with XRD results where it is proven that crystals have relative large size.
4. Conclusion
Silica from elephant grass was successfully isolated, the results of characterization using EDX showed the composition of SiO$_2$ as much as 71.91%. The isolated silica has an amorphous phase and was used as precursor for the synthesis of silicalite-1 zeolite. The results of XRD and FTIR measurements showed that silikalit-1 zeolite was successfully synthesized, SEM characterization showed hexagonal morphology in a non-uniform size.

Acknowledgement
We acknowledge LP2M UIN Sunan Gunung Djati Bandung provided financial support.

References
[1] Syahroel 2017 Material Science [Online] Retrieved from: http://www.material-sciences.html
[2] M Tsujiguchi, T Kobashi, J Kanbara and Y Utsumi 2013 Synthesis of Zeolite from Glass 62 6 357–361
[3] Y Peng, X Lu, Z Wang and Y Yan 2015 Fabrication of b -Oriented MFI Zeolite Films under Neutral Conditions without the Use of Hydrogen Fluoride 5709–5712
[4] A H Mukaromah, M Amin and R R Mukti 2017 Pengaru Variasi Mol H$\text{H}_2$O terhadap krisinalinizitas Zeolit ZSM-5 4–8
[5] J J Ekputuri 2013 Sodium sebagai Aktivator Fly Ash , Trass dan Lumpur Sidoarjo dalam Beton Geopolimer 20 1 1–10
[6] K Kordatos, S Gavela, A Ntzoumi, K N Pstiosla and A Kyritsi 2008 Synthesis of highly siliceous ZSM-5 zeolite using silica from rice husk ash 115 189–196
[7] C D D Sundari, S Setiadji, Y Rohmatullah, S Sanusi, D F Nurbaeti, I Novianti, I Farida, A Nurohmah, and A L Ivansyah 2018 Synthesis of zeolite L using rice husk ash silica for adsorption of methylene blue: kinetic and adsorption isotherm MATEC Web of Conferences 197 05002
[8] S Setiadji, C D Dewi Sundari, E Lala, D F Nurbaeti, I Novianti, D Suhendar, W Darmalaksana and A L Ivansyah 2018 The increased use value of bamboo leaves as silica source for t-type zeolite synthesis MATEC Web of Conferences 197 05003
[9] S Setiadji, I S Nuraziah, C D D Sundari, W Darmalaksana, D F Nurbaeti, I Novianti, T B N Azizah, D Abdurrahman, A L Ivansyah 2018 Synthesis of zeolite ZSM-11 using bamboo leaf as silica source IOP Conference Series: Materials Science and Engineering 434 (1) 012084
[10] C D D Sundari, S Setiadji, A L Ivansyah, D Abdurrahman, D F Nurbaeti 2018 Ag-ZSM-11 Zeolite Synthesis Using Silica from Elephant Grass for LED Application Walisongo Journal of Chemistry 2 2
[11] E Rustiyananaa, Limanb and F Fathulb 2016 Effect of Substitution of Elephant Grass (Pennisetum purpureum) with Palm Leave Sheat on the Digestibility of Crude Protein and Crude Fiber
Digestibility in Goats 4 2 161–165

[12] A Retnosari 2013 *Ekstraksi dan Penentuan Kadar Silika (SiO2) Hasil Ekstraksi dari Abu Terbang (Fly Ash) Batu Bara*

[13] V A Fabiani 2014 *Pengurangan Agen Pengaruh Struktur Sintesis Zeolit ZSM-5 Menggunakan Prekursor Silika Alam*

[14] K P Dey, S Ghosh and M Kanti 2013 Organic template-free synthesis of ZSM-5 zeolite particles using rice husk ash as silica source 39 2153–2157

[15] P Velmurugan 2015 *Extraction, characterization, and catalytic potential of amorphous silica from corn cobs by sol-gel method 29*

[16] S Sulastri and S Kristianingrum 2010 *Berbagai Macam Senyawa Silika: Sintesis, Karakterisasi dan Pemanfaatan* 211–216

[17] S Yusri 2012 Sintesis dan Karakterisasi Zeolit ZSM-5 Mesopori dengan Secondary Template dan Studi Awal katalisis Oksidasi Metana

[18] F Yaripour, Z Shariatinia, S Sahebdelfar, and A Irandoukht 2015 Journal of Natural Gas Science and Engineering Conventional hydrothermal synthesis of nanostructured H-ZSM-5 catalysts using various templates for light olefin production from methanol *J. Nat. Gas Sci. Eng.* 22 260–269