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Extraction of silica from cogon grass and utilization for synthesis of zeolite NaY by conventional and microwave-assisted hydrothermal methods

Komsan Bunmai[a], Nattawut Osakoo[a,*], Krittanun Deekamwong[a], Wina Rongchapo[a,b], Chalermpan Keawkumay[a], Narong Chanlek[c], Sanchai Prayoonpokarach[a], Jatuporn Wittayakun[a,*]

[a] School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand
[b] School of Environmental Health, Institute of Public Health, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand
[c] Synchrotron Light Research Institute SLRI, Nakhon Ratchasima 30000, Thailand

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ABSTRACT

High purity silica is obtained after leaching glassy blade and trunk of cogon grass in HCl acid with various concentrations (1.5, 2.0, 2.5 and 3.0 M) and calcination at 500 °C for 4 h. The silica yield from the blade from all acid-leached samples is around 9 wt%, higher than that from the trunk (around 4 wt%). The sample leached with 2 M HCl has the highest silica purity (99.34 ± 0.02 wt%) and is further used in the syntheses of zeolite NaY by conventional and microwave-assisted hydrothermal methods (CH and MH). The NaY-CH has a larger particle size, BET surface area and total acidity than that NaY-MH. Interestingly, the NaY-MH has a larger external surface area and stronger acid strength.

1. Introduction

Imperata Cylindrica, commonly known as cogon grass, a weed widely found in Thailand, is seldom considered useful [1]. It is usually removed by burning which leads to air pollution. However, the cogon grass is suggested as a source of hydrated silica [2].

In general, high purity silica can be obtained from biomass by acid leaching to remove any containing minerals followed by calcination in air [3]. Silica content in glassy blade of cogon grass in Malaysia is reported by Kow and coworkers [4]. However, the silica content in the grass trunk is not yet explored and becomes an interest of this work.

Amorphous silica powder is employed in several applications such as a starting material for zeolite synthesis, absorbents, aerogel, electronic devices, solar cell as well as in cement industry [4]. In the last decade, high purity silica from rice husk was utilized in the syntheses of micro and mesoporous materials [3,5,6]. However, the use of silica from rice husk seems to decline because the rice husk itself can be used as a cheap energy source through combustion to produce electricity [7,8]. Thus, the use of other sources like cogon grass as an alternative renewable silica source is interesting due to its low commercial value.

To further correlate to catalysis research, the silica from rice husk is employed for the synthesis of zeolite Y in sodium form (NaY), one of the most used zeolites [3,9] in various applications including catalyst support for transesterification, cracking catalysts and adsorbent [10,11,12].

Zeolite NaY can be synthesized by a conventional hydrothermal (CH) method which is a slow process. There are reports that an application of microwave irradiation could shorten the zeolite synthesis time [13,14]. From the work of Katsuki and coworkers [13], NaY is synthesized from colloidal silica by microwave-assisted hydrothermal (MH) method at 100 °C within 2 h. Its BET surface area is similar to the NaY synthesized by the conventional hydrothermal method at the same temperature but with a longer time.

To our knowledge, there are no reports on properties of zeolite NaY synthesized by CH and MH methods using silica from cogon grass. Therefore, the aims of this work are to study the effect of acid concentration on the purity of silica obtained both from the glassy blade and trunk of the cogon grass in Thailand and properties of zeolite NaY synthesized from cogon grass by CH and MH methods.

* Corresponding authors.
E-mail addresses: nattawut.work@gmail.com (N. Osakoo), jatuporn@sut.ac.th (J. Wittayakun).

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2. Experimental

2.1. Materials

Fresh cogon grass including glassy blade and trunk is obtained from a grassy field around Suranaree University of Technology (Nakhon Ratchasima, Thailand). Chemicals used in this work are sodium aluminate (95%, Sigma-Aldrich), sodium hydroxide (97%, Carlo Erba), hydrochloric acid (37%, Merck).

2.2. Silica extraction

The fresh cogon grass is cut, washed thoroughly with water to remove the adhering soil and dust and dried outdoor for 30 days. Then, the grass blades and trunks are cut to the length of 3–4 mm, washed with deionized water (DI) several times and dried in an oven at 90 °C for 120 h. A 30 g of the dried blade or trunk is refluxed in 400 mL of HCl solution with varied concentrations (1.5, 2.0, 2.5, 3.0 M) at 90 °C for 3 h, cooled down, filtered and washed with DI water until the filtrate is neutral, dried at 90 °C and calcined at 500 °C for 4 h. The yield of silica powder is calculated by Eq. (1).

$$\text{Yield of silica powder} = \frac{\text{weight of calcined cogon grass}}{\text{weight of dried cogon grass}} \times 100 \quad (1)$$

2.3. Synthesis of zeolite NaY by conventional and microwave-assisted hydrothermal methods

Zeolite NaY is synthesized by CH method from a seed gel and feedstock gel with a method adapted from the literature [3,15]. The seed gel with a molar ratio of $10.67Na_2O$: Al_2O_3:$10SiO_2$:$180H_2O$ is prepared, stirred and transferred into a 25 mL-polypropylene (PP) bottle, capped, and aged at ambient temperature for 24 h. Afterward, the feedstock gel with molar ratio $4.30Na_2O$: Al_2O_3:$10SiO_2$:$180H_2O$ is prepared and used immediately without aging by adding to the seed gel under stirring. The final mixture is transferred to a PP bottle, capped, and crystallized at 100 °C for 24 h.

Zeolite NaY is synthesized by microwave-assisted hydrothermal method (MH) with a method from the literature [3,13]. The composition of seed gel and feedstock gel is prepared with a similar method mentioned above. The final mixture is treated at 100 °C for 2 h in a vessel lined with Teflon (X press Plus) employing in a microwave digestion system with the frequency 250 GHz and power 300 W (Model CEM, SPD). The solid product from both methods is separated by centrifugation, washed with DI water and dried at 110 °C for 12 h.

2.4. Characterization of silica from cogon grass and zeolite NaY

Phases of calcined products from acid-leached cogon grass, NaY and calcined NaY at 800 °C for 1 h are studied by X-ray diffraction (XRD, Bruker D8 ADVANCE) using Cu Kα X-ray generated with a current of 40 mA and a potential of 40 kV. The same sample weight (0.35 g) is used and the samples are analyzed in the same day, thus, the crystallinity can be compared with more confidence. Morphology of cogon grass, silica powder and NaY zeolite is analyzed by scanning electron microscopy (SEM, JEOL JSM-6010 LV and JSM-7800F). Elemental compositions of silica from cogon grass are determined by using inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 8000) and energy dispersive X-ray fluorescence (ED-XRF, Oxford ED2000). Before analysis by ICP-OES, 50 mg of each sample is digested in 0.5 mL aqua regia of 65% HNO_3 and 37% HCl with the volumetric ratio of 1:3 and 3.0 mL of 48% HF at 110 °C for 1 h. Then 2.8 g of boric acid and 10 mL of DI water are added to the mixture. Afterward, the mixture volume is adjusted to 100 mL in PP volumetric flask. To screen combustion temperature in air, cogon grass (blade) refluxed in 2.0 M HCl, is heated from room temperature to 800 °C at a heating rate of 10 °C/min under a 50 mL/min of air zero (Fig. S1 in Supplementary Materials). Thermal decomposition of silica from cogon grass and NaY zeolite is studied by a thermogravimetric analysis (TGA, Mettler TGA/DSC1). The samples are heated from room temperature to 800 °C at a heating rate of 10 °C/min under a 50 mL/min of nitrogen. Sorption properties of silica and NaY are analyzed by N_2 adsorption–desorption on a BELSORP-mini II at liquid nitrogen temperature. Prior to the analysis, the samples are degassed at 300 °C under vacuum for 24 h. Acidity of synthesized NaY is determined by temperature-programed desorption of ammonia (NH_3-TPD) on a BELCAT-B with a procedure reported in the literature [16]. In addition, Si/Al ratio of framework zeolite is analyzed by X-ray photoelectron spectroscopy (XPS, ULVAC-PHI, PHI 500 VersaProbe II) using Al Kα radiation with a procedure reported in the literature [17].

Table 1
Solid yield after calcination based on the grass dried weight and chemical composition determined by ICP-OES.

	Yield (% wt)	Composition (% wt.)				
		Al_2O_3	SiO_2	K_2CO_3	Fe_2O_3	$CaCO_3$
Trunk						
no reflux	3.57	0.63	67.63	14.10	0.14	17.49
1.5 M	3.59	0.30	97.77	0.27	0.08	1.57
2.0 M	3.68	0.25	98.46	0.19	0.03	1.06
2.5 M	3.63	0.18	97.90	0.29	0.04	1.58
3.0 M	3.80	0.18	97.83	0.24	0.04	1.69
Blade						
no reflux	8.59	0.58	70.34	7.01	0.07	21.98
1.5 M	9.05	0.47	97.93	0.10	0.02	1.46
2.0 M	9.45	0.33	99.34	0.04	0.01	0.27
2.5 M	9.11	0.33	97.66	0.24	0.02	1.74
3.0 M	9.90	0.22	98.01	0.04	0.03	1.70

3. Results and discussion

3.1. Phase, composition and morphology of silica from cogon grass

As shown in Fig. 1a and 1b, the calcined trunk and blade of cogon grass before acid leaching exhibit a broad peak at 22° and sharp peaks at 29°, 38.5°, 43.59° and 48.17° The broad peak corresponds to a characteristic of amorphous silica and the sharp peaks correspond to $CaCO_3$ [18]. After leaching in acid with various concentrations, the calcined trunk and blade of cogon grass show a broad peak at 22° indicating that amorphous silica is the main phase. A small peak at 29° is observed from some samples indicating a trace of $CaCO_3$. The amorphous silica from cogon grass is suitable for zeolite synthesis because it dissolves expediently in NaOH solution [3].

As revealed in Fig. 2a and 2b, a slightly different morphology is observed from the dry blade before and after leaching with 2.0 M HCl. Small needle-like furs on the surface are removed by acid leaching. Results from elemental analysis with ED-XRF and elemental mapping indicate that carbon is a major component. This data agrees with the literature that cellulose content in cogon grass is 37.2% [19]. Other compounds containing Ca and K are observed in the dry samples but removed by acid leaching. In addition, Si contents in both samples are similar.

As listed in Table 1, solid yields after calcination from the trunk and blade are around 9 wt% and 4 wt%, respectively. The major component of all samples is silica. For untreated samples, the blade

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