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Modification of Gunungkidul Natural Zeolite as Bioethanol Dehydrating Agents

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Abstract

This research was conducted to characterize the modification of natural zeolite for dehydration of bioethanol. Modification have been conducted under various methods. Natural zeolite (ZA) was activated using hydrochloric acid (produced ZAAH), the ZAAH sample was heated in to microwave (produced ZAAHM), soaking of ZAAH and ZAAHM in NH_4NO_3 (produced ZAAHN and ZAAHMN). Zeolite characterization involved determination of total acid sites, zeolite crystallinity by X-ray diffraction and TO_4 site by FTIR. Result showed that modified zeolite ZAAH have better properties compared by ZA, ZAAHM, ZAAHN and ZAAHMN. ZAAH potentially be used as dehydrating agents.

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Keywords: bioethanol; dehydration; Gunungkidul natural zeolite; microwave.

Nomenclature

ZA	natural zeolite
ZAAH	modified zeolite by acid treatment
ZAAHM	modified zeolite by acid and microwave treatment
ZAAHN	modified zeolite by acid and ammonium nitrate treatment
ZAAHMN	modified zeolite by acid, ammonium nitrate and microwave treatment
h	hour
min	minute
t	ton = 10^3 kg

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1. Introduction

Anhydrous ethanol production has become to be one of the most important issues for many countries in the world due to the great efforts directed to use biofuels and diminishment in pollution and environmental effects of fossil fuels. The process of anhydrous alcohol production comprises three main important steps: fermentation, distillation and dehydration. In the final dehydration step the quality of ethanol is determined by the operating conditions, the technology used and its benefits related to the quality and costs of ethanol [1].

To produce ethanol at a high level of dryness, adsorption process on zeolite material has proven to be ideal. There have been several researches on adsorption of water from ethanol-water mixture using zeolite media. Most of these researchers studied the adsorption of ethanol in vapor phase and/or liquid phase using some common commercialized zeolite material [2]

Zeolites are the best adsorber for the adsorption process [3].The zeolite utilization as adsorber due to the porous structure, molecular sieve and absorbing ability for small molecules such as water which can enter the zeolite [4]. There are about 40 types of natural zeolite, although which has commercial value about 12 types, including clinoptilolite, mordernit, filipsit, kabasit and erionite [5].

On the other hand, there are widespread, abundant resources of natural zeolites in Indonesia. Their utilization as absorber, however, has been little explored, in spite of the fact that their potential effectiveness may contribute to reduce industrial production costs. Modifications of the natural zeolite are needs to be done to improve their performance before used as an adsorbent. The zeolites showed better performance in crystallinity and acidity after treated with HCl [6].

In an attempt to utilized Indonesian natural zeolite as adsorbent, in the present the authors undertaken modification of natural zeolite produced in Gunungkidul, Indonesia, which have appeared to consist mainly of mordenite type crystalline matter, and its modifications by treating with an aqueous HCl solution, followed by microwave treatment. Their properties bioethanol dehydration agents were characterized. The results described in the following section.

2. Material and method

2.1. Material

Natural zeolite (ZA) was obtained from Gunungkidul, Indonesia. ZA was ground and sieved to < 100 mesh particles before use. The material was used throughout the research to obtained reproducibility and consistent results.

2.2 Treatment of zeolite

About 50 g of natural zeolite sample in 3 N HCl (100 cm^3) was heated at 90 ºC for 24 h min while magnetically stirred. After the HCl treatment, the sample was filtered and washed with deionized water until no chloride ion could be detected by test using $AgNO_3$ solution, after which it was dried at 110 ºC for 3 h and calcined at 450 ºC for 3 h. This sample was coded as ZAAH. The ZAAH sample was then heated in a microwave at 550 watt, 90 ºC for 10 min produced the ZAAHM sample. The ZAAH and ZAAHM were then immersed in 1 N NH_4NO_3 solution for 24 h at room temperature while mild stirring. After the treatment the sample was then filtered and washed with deionized water, after that it was dried at 120 ºC for 3 h. The resulting sample were coded as ZAAHN and ZAAHMN

2.2 Characterization of zeolite

The effect of modified treatments towards dealumination (TO_4 sites) as well as acid sites in the natural zolite was analyzed by FT-IR spectrophotometer (Shimadzu). Total acid site amount on zeolite samples was determined gravimetrically using ammonia and pyridine base vapour adsorption. Crystallinity changed of zeolite samples was analyzed by XRD (Shimadzu), and their specific surface area by Quantachrome Instruments.

The infrared spectra (4 000 cm^{-1} to 400 cm^{-1}) were recorded on Shimadzu Prestige-21 FT-IR Spectrophotometer using the KBr pellet technique. The samples were mixed thoroughly with potassium bromide, an infrared transparent matrix, at 1 : 5 (sample : KBr) ratio, respectively. The KBr discs were prepared by compressing the powders at a pressure of 5 t for 5 min in a hydraulic press. The thin discs were placed in a ring-type sample holder and transferred into the IR cell equipped with CaF_2 window and then attached to the vacuum system (1 x 10^{-8} mbar).

X-ray diffractogram of zeolites were performed using X-Ray diffractometer (Shimadzu). The cross section of samples was exposed to x-ray radiation (Cu Kα) with wavelength of 1.540 6 A at 40 kV and 30 mA. The rate of the scanning was 0.6^o/min at a range of 5^o to 50^o 2θ and vertical goniometer at room temperature. Samples were grounded into powders with an agate mortar and pestle, then measured on a low background quartz plate in an aluminum holder.

The nitrogen adsorption isotherms were obtained at liquid nitrogen temperature using a Quantacrome Instruments that used a static volumetric technique. The instrument was home-modified by adding two pressure gauges working in the range (0 to130) Pa and (0 to13) kPa in order to more accurately measure the low-pressure value

3. Results and discussion

In previous study, Wahono et al. [7] reported have modified Gunungkidul natural zeolite and use it as a dehydrating agent for bioethanol. The results showed that the modified natural zeolite has ability to purify bioethanol relatively similar to the commercial zeolite (purity more than 99 %) but has lower yield. Therefore, in the present paper, effect of hydrocloric acid, microwave and ammonium nitrate for the modification of Gunungkidul natural zeolite were investigated, and their properties were characterized. The results described in the following section.

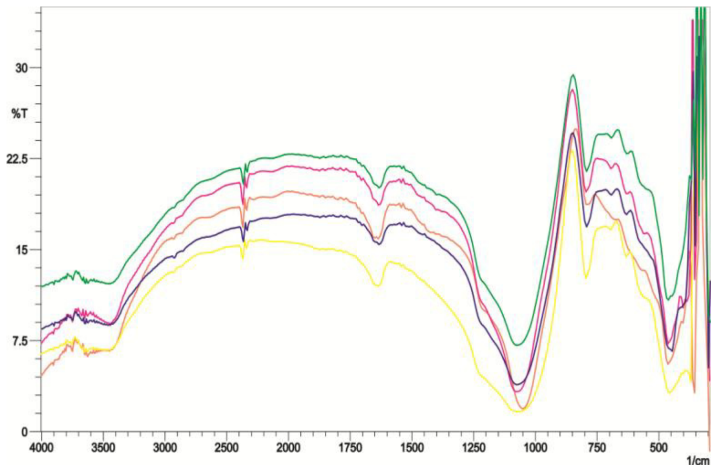

Fig. 1 FTIR spectrograms of ZA (orange); ZAAH (yellow) , ZAAHM (blue), ZAAHN (purple), ZAAHMN (green)

Effect of the modified treatment towards zeolite framework was characterized by FTIR based on the wave number of TO_4 (T = Si or Al) site at (1 250 to 950) cm^{-1} . The structure sensitive absorption around (1 200 to 550) cm^{-1} is of special interest to distinguish the zeolite types [8]. The result was shown in Fig. 1. All samples have vibration bands at (546 to 1 223) cm^{-1}. Fig. 1 showed that the acid treatment caused dealumination of the zeolite sample indicated by the shifted of the wave number from (1 049.28 to 1 072.42) cm^{-1}. This frequency band is assigned to the asymmetric stretching of framework Si–O–Si or Si–O–Al bonds. The acid treatment leached Al framework [9,10] of Gunungkidul natural zeolites. Microwave treatment enhanced the dealumination caused by the wave that activated the movement of Al out from the zeolite framework [11]. The successive treatment (acid treatment, microwave treatment) caused the increase of dealumination.

Table 1 Total acid and surface acid on zeolite

Sample	Ammonia (mmol · g^{-1})	Pyridine (mmol · g^{-1})
ZA	0.907	0.629
ZAAH	1.398	0.672
ZAAHM	1.361	0.680
ZAAHN	1.394	0.642
ZAAHMN	1.358	0.648

Zeolite acidity is necessary to characterize for determine the number and strength of both types of acid sites, Brönsted acid and Lewis acid [12]. Table 1 showed total acid amount of the zeolite samples determinated by ammonia or pyridine base vapour adsorption. It can be seen that the acid amount determined by ammonia was higher than that of pyridine. This phenomena caused by the facts that ammonia was a stronger base than that of pyridine and pyridine has bigger molecular size than ammonia thus pyridine can only adsorbed in the outer surface of the zeolite. Ammonia with smaller molecular size can be adsorbed on outer and inside the zeolite surfaces. It can also be seen that the total acid amount of the zeolite samples increased by the treatment orders. These may be caused by the dissapearance of impurities in the zeolite**.**

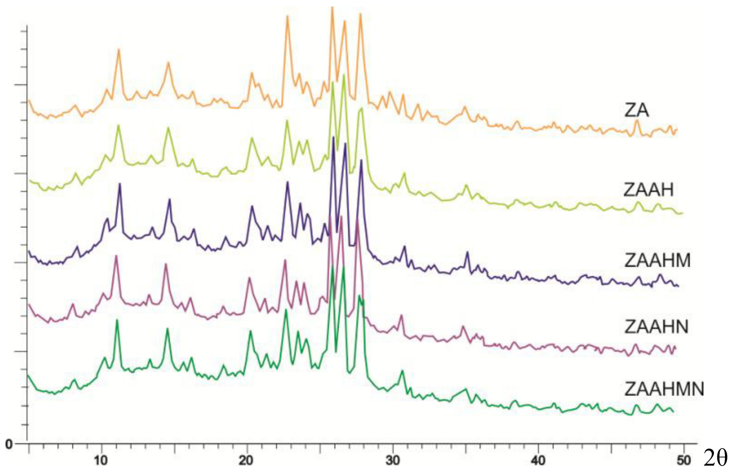

Fig. 2 Zeolite XRD patterns of ZA (orange); ZAAH (light green) , ZAAHM (purple), ZAAHN (pulm), ZAAHMN (green)

X-ray difraction provides information about crystallinity of the zeolites, as shown on the XRD difractograms (Figure 1). The difractograms revealed that there is no change in the ZA and modified zeolite (ZAAH, ZAAHM, ZAAHN, ZAAHMN) crystalline structure after modifcation treatment. The peaks at 2θ values of 25.4^o and 29.2^o are single peaks for ZA and modified zeolite samples, indicating that the structure of the samples did not change from orthorhombic to monoclinic after the modification.

Table 2.Surface area, pore volume and average pore size of zeolite

Sample	Surface area ($m^2 \cdot g^{-1}$)	Pore volume (cc · g^{-1})	Average pore size (Å)
ZA	21.504	4.828 e^{-2}	4.491
ZAAH	115.842	9.703 e^{-2}	1.675
ZAAHM	107.164	1.007 e^{-1}	1.880
ZAAHN	79.253	8.733 e^{-2}	2.204
ZAAHMN	79.553	8.448 e^{-2}	2.124

The isotherm adsorption of natural zeolite and modified zeolite provided the pore distribution data. The presence of a hysteresis loop is associated with capillary condensation, where in the case of zeolite, it indicates the formation of mesopores (secondary pores). The surface area, pore volume and average pore size of the samples are given in Table 2. From Table 2, the ratio of BET surface area for ZA samples have vary a great deal after modification. The values obtained are within experimental error. However, the BET surface area ratio of ZA to ZAAH, ZAAHM, ZAAHN, ZAAHMN respectively increases by 538.7 %, 498.3 %, 368.5 %, 369.9 %. This suggests that acid treatment followed by calcination, microwave treatment caused the increase of dealumination and disappearance of impurities.

4. Conclusion

Gunungkidul natural zeolite modified by acid treatment followed by calcination (ZAAH) has the better properties than ZA, ZAAHM, ZAAHN and ZAAHMN. ZAAH has a surface area 115.842 $m^2 \cdot g^{-1}$ (five times more than ZA), pore volume of 9.703 e^{-2} $cc \cdot g^{-1}$, average pore size of 1.67522 (Å) and total acid of 1.398.

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