

Natural Zeolite Catalyst for Conversion of α -Pinene

Wijayati N. and Utomo A. B.

Abstract—The Natural zeolite catalyst (Si/Al = 2.5) was prepared by calcination. The physico-chemical properties were investigated by XRD, ^{29}Si MAS NMR, SEM, GC-MS and FT-IR spectroscopy of pyridine adsorbed. The activity of test of these catalysts has been carried out over the liquid-phase conversion of α -pinene. The conversion reaction with natural zeolite, the highest selectivity of terpin compound was 59.08% with a conversion of 99.78% at 120 min.

Index Terms—Natural zeolite, α -Pinene, conversion.

I. INTRODUCTION

Zeolite material is available so much in Indonesia because most areas in Indonesia are volcanic mountain, which is source of Zeolite minerals. According to the geologist's research, there has been found 47 location of zeolites mining in Indonesia, the three are in East Java is Sumbermanjing-Wetan, Kedung Banteng village and Sumber Agung village in South Malang and Slaung Ponorogo, approximately have million tons stocks.

Zeolites are natural or synthetic crystalline, microporous, aluminosilicate materials with structures consisting of three dimensional frameworks of SiO_4 and AlO_4 tetrahedra linked through oxygen bridges [1]. Zeolite solid acidity make it useful as ion exchange, adsorption, heterogeneous catalysis, biosorption supports, polymer catalytic degradation and also attract interest in materials science for the development of functional materials and in nanotechnology [2]-[5].

The conversion reaction of α -pinene in the presence of zeolite catalyst has been well studied, and intensely so in the last ten years. Mochida *et al.* [7] reported the use of zeolites and obtained 100% conversion, but with low selectivity for alcohols (around 57%).

The wealth of experimental material has attracted the attention of theoreticians for decades. The whole spectrum of intrazeolite phenomena such as 1) diffusion of reactants into the zeolite, 2) physisorption (chemisorption) at the active site, 3) reaction of the conversion, 4) desorption, and 5) diffusion out of the zeolite [8].

Based on the statement above, the use of zeolite because of the big enough relatively of adsorption capacity and state use in cattle raising and medical. So that need the development of the use of zeolite as new adsorbent raw material. This paper describes the characterization of the natural zeolite catalyst and the use in the conversion of α -pinene as catalyst.

II. PROCEDURE

A. Experimental

The catalysts were characterized by XRD, ^{29}Si MAS NMR, SEM, GC-MS and FT-IR spectroscopy of pyridine adsorbed. X-Ray Diffractometer (D-Max III (Rigaku), radiation $\text{Cu K}\alpha$ ($\alpha = 1.5378 \text{ \AA}$, 40kV, 30mA). The NMR spectra were obtained at 9.4 T on a Bruker DRX-400 spectrometer using 4mm ZrO_2 rotors at room temperature. ^{29}Si MAS NMR spectra with high power proton decoupling was obtained at 79.49MHz with a spinning rate of 12 kHz, pulse length of 3 μs and a recycle time of 20 s. 4 mm rotors was used and the ^{29}Si chemical shifts was reported relative to TMS. The morphology and mean crystallite size of the zeolites was determined by scanning electron microscopy (SEM) in a JEOL JFC-1600 and JSM-6701F equipment. 1) Pt auto fine coater, Model: JEOL JFC-1600; Parameters: 20mA, 30sec coating time; Pt thickness: approx. 5nm. 2) FESEM. Model: JEOL JSM-6701F Voltage range: 0.1 - 30kV, Magnification: 25X-650kX, Resolution: 1nm by specification. The IR spectroscopy of pyridine adsorbed (Py-IR) was carried out on a (Hitachi 270-50; Perkin Elmer Paragon 1000 PC; Shimadzu FTIR-8201PC). GC-MS instrument (Agilent GC/MSD (7890A/5975C). The column used was DB-5MS 27m \times 0.25mm \times 0.25 μm B-5, Mass range: 41-500amu, Carrier gas flow rate: 1ml/min, Injector temperature: 260°C; Temperature program: 50°C(2min)-260°C(5min), heating rate 5°C/min; Flow: 1 mL/min; split ratio: 20. Note: 3 μL of sample TP diluted with 1mL of methanol for GCMS analysis.

B. Preparation of Catalyst

Natural zeolite was calcined by flowing nitrogen, oxidized by oxygen, and reduced by hydrogen gases. Characterizations of catalysts including acidity test, determination of crystallinity, and metal content were carried out respectively by using pyridine adsorption, XRD, SEM and ^{29}Si MAS NMR.

C. Catalytic Test

Acid catalyzed hydration reaction of α -pinene was conducted using bath reactor of 100 mL three-neck flask with condenser, a sample and a thermometer. A mixture of 1.84 mmol of α -pinene, 2.5 mL of H_2O , and 3.4 mL of isopropyl alcohol was loaded into reactor. The mixture was stirred and warmed up to the desired temperature. Once the desired temperature was reached, the 400 mg of natural zeolite catalyst was added into the reactor. The reaction products were analyzed by GC by taking samples at 30, 60, 120, and 240 min after the addition of catalyst. The samples were centrifuged at high speed of rotation (350 rpm) for about 10 min at ambient temperature to ensure that they were free of solid catalyst. Peak identification of the products was done by GC-MS analysis.

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III. RESULT AND DISCUSSION

A. Acidity Test of Natural Zeolite Catalyst

Acidity test was conducted by ammonia and pyridine adsorption. Ammonia and pyridine were chosen as adsorbates because they are small molecules allowing them to be adsorbed not only on the surface but also in the zeolite channels. In addition, ammonia can also act as Lewis and Brønsted bases so that the total acidity can be determined well. Determination of acidity of the catalyst with pyridine used to determine the Lewis acid sites only, because pyridine can only act as a Lewis acid alone (see Fig. 1).

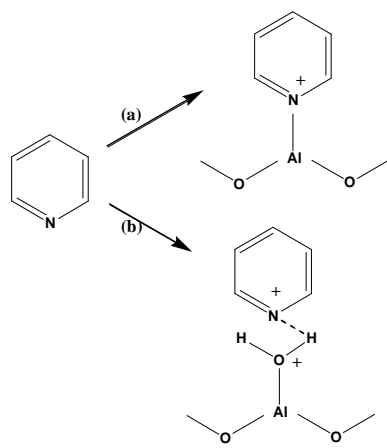


Fig. 1. Interaction of pyridine (a) Lewis dan; (b) Brønsted acid sites from natural zeolite catalyst.

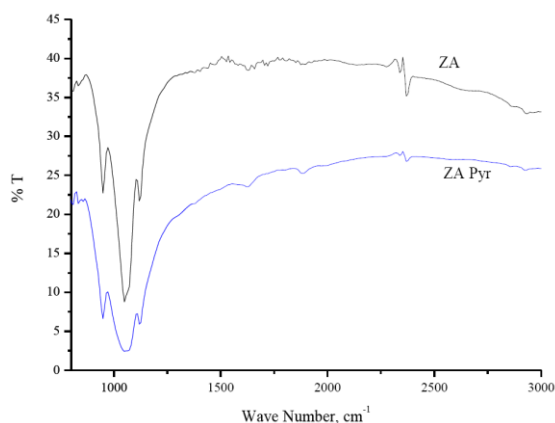


Fig. 2. FT-IR spectra of natural zeolite.

B. FT-IR Analysis

The amount of Brønsted and Lewis acid sites of the studied samples, as determined by pyridine adsorption (Py-IR), are shown in Fig. 2. Py-IR spectra of two characteristic absorption peaks, of which 1543 cm^{-1} and 1442 cm^{-1} , attributable to pyridine adsorbed on Brønsted acid and Lewis acid sites, respectively [11], [12].

C. XRD

The X-ray powder diffraction (XRD) patterns of natural zeolite was shown in Fig. 3. The XRD patterns show that the sample was zeolites topology, well crystallined and are free from impurities. The result show that zeolite mining rock Malang, contains kinds of Mordenite.

D. ^{29}Si MAS (Magic Angle Spinning) NMR

The ^{29}Si MAS NMR spectra of the natural zeolite samples are shown in Fig. 4. It is well known that a ^{29}Si MAS NMR spectrum of the natural zeolite may contain up to five lines

depending on the number of aluminum atoms and silanol groups connected to the silicon atom [9], [10]. The ^{29}Si MAS NMR spectrum of the natural zeolite sample shows the presence of four components, corresponding to Si(0Al), Si(1Al), Si(2Al) and Si(3Al) species at -108 , -102 , -99 , and -94 ppm, respectively, similar to that observed by Yan *et al.*, [9].

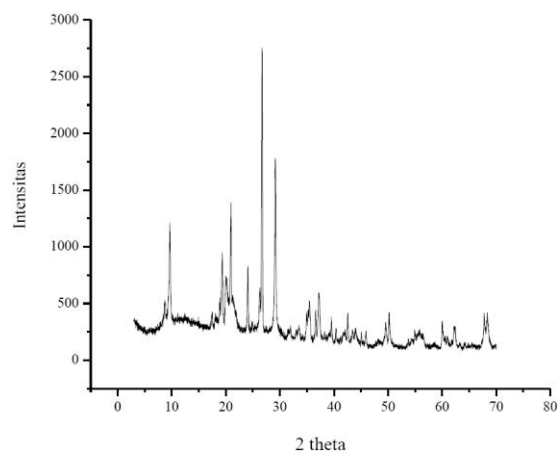


Fig. 3. XRD pattern of natural zeolite catalyst.

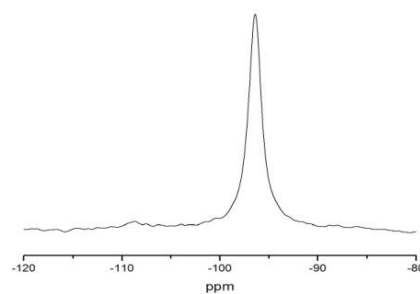


Fig. 4. ^{29}Si MAS NMR spectrum of Natural Zeolite.

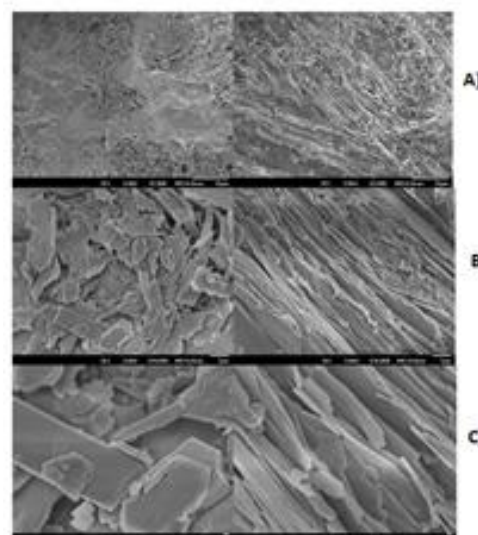


Fig. 5. SEM image of ZA different magnifications (A) $10\ \mu\text{m}$, (B) $1\ \mu\text{m}$, and (C) $100\ \text{nm}$.

E. SEM

Scanning electron microscopy (SEM) concludes that the morphology of the outer surface of the natural zeolite crystals (see Fig. 5).

F. Catalytic Activity

Catalytic study was performed using natural zeolite. The

molecular size of α -pinene was estimated to be $0.62 \times 0.59 \times 0.53$ nm, which is smaller than natural zeolite catalysts [7]. The reaction was carried out in an excess of water with α -pinene as the limiting reagent. α -Pinene was almost immiscible in water at the reaction conditions. It forms a separated organic phase in the reactor. The reaction takes place over the catalyst surrounded by the aqueous phase. α -Pinene should adsorb on acid site to promote the acid catalyzed reaction in the presence of water [13].

Effect of reaction time on the α -pinene conversion and selectivity of product for natural zeolite catalyst was shown in Fig. 6.

To achieve a well mixing between the reagents and the α -pinene during reaction, they must be stirred well at constant rate. The observed conversion of α -pinene with natural zeolite was observed from 30 min until 240 min. The highest selectivity of terpene compound was 59.08% with a conversion of 99.78% at 120 min.

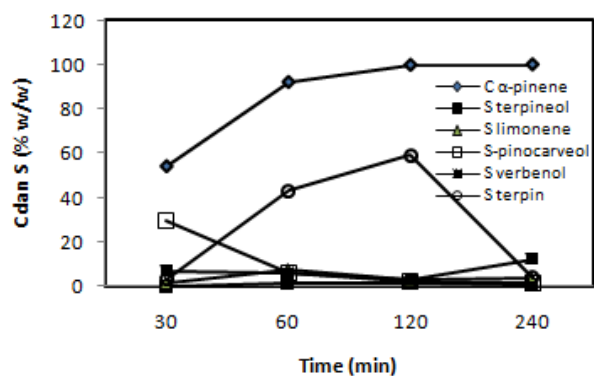


Fig. 6. Conversion and selectivity of product vs. reaction time. S= Selectivity; C= Conversion

Fig. 6 shows that the main products were α -terpineol, limonene, pinocarveol, verbenol, and terpene. Castanheiro, *et al.* [13] proposed reaction scheme for the acid catalyzed conversion of α - and β -pinene. They used molybdophosphoric acid as catalyst and obtained limonene, α -terpineol and terpene as main products. This selectivity (Fig. 7) consists of a subtle matching of the size and shape of reactants, transition states and products with the zeolite framework [14].

IV. REACTANT SHAPE SELECTIVITY

The acid catalyzed the conversion reaction of alkenes in aqueous solution. The acid transfers a proton to double bond of the alkene forming an intermediate of carbocation. The carbocation can lose a proton and generate monocyclic and bicyclic hydrocarbons or, in the presence of a nucleophile, give to monocyclic alcohol. In the conversion of terpenes, various products might be obtained depending on the catalyst and reaction conditions [6]-[13].

The catalyst of natural zeolite was studied for this conversion reaction. The internal surface of catalyst being highly hydrophobic possesses affinity towards non polar molecules like that of α -pinene [7]. Natural zeolite has high activity for α -pinene conversion, indicating the high potential of this catalyst as an alternative solid acid catalyst to

conventional homogeneous catalyst. By evaluating this work, it was a good candidate for the industrial conversion of α -pinene, due to its easy separation from reaction products and low cost.

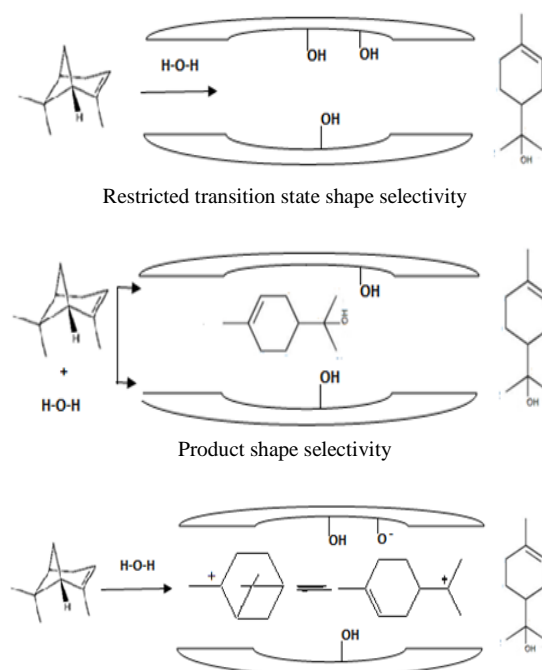


Fig. 7. The three classic types of shape selectivity.

V. CONCLUSION

XRD and SEM show that the natural zeolite nanocrystals obtained are highly crystalline, contains kinds of Mordenite. The Si/Al ratio of natural zeolite was 2.5. The natural zeolite was a good candidate for the industrial conversion of α -pinene, due to its easy separation from reaction products and low cost. The conversion of α -pinene catalyzed by natural zeolite was fast and leads mainly to terpene as the major product (up to 59%).

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