

MODIFIED DESILICATED NATURAL ZEOLITE CATALYST FOR KNOEVENAGEL REACTION

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Abstract

Natural zeolite (NaZ) has wide range of usage in agriculture and waste water treatment. However, its application as catalyst has not been widely studied. In this research, natural zeolite was modified its property and applied as base catalyst in the Knoevenagel reaction. The modification was done by desilication in alkaline solution at different temperature followed by ion exchanged with calcium and barium ions of alkaline earth metal. The natural zeolite obtained characterized with XRD showed that desilication results in lowering crystallinity of zeolite crystal while FT-IR showed Si/Al ration of the zeolite framework decrease showing the increase of Al in the framework. The catalyst produced was then tested in Knoevenagel reaction and analyzed by gas chromatography (GC) which showed that barium exchanged desilicated NaZ is more active and highly selective than calcium exchanged NaZ due to its higher basicity.

Keywords: natural zeolite, mordenite, desilication, ion exchange and Knoevenagel reaction

INTRODUCTION

Zeolite is an inorganic crystalline, hydrated alluminosilicate of alkaline and alkaline earth cation consists of infinitely extending 3 dimensional networks of AlO_4^{5-} and SiO_2^{4-} tetrahedral which is linked by oxygen [1]. It has been discovered as a potential material in various industrial applications because it can prevent pollution, environmental friendly substance, conserve raw material and low in production. It can be found in naturally and can be synthesized. Zeolite has a varied application due to its unique characteristic which are the microporous structure that give uniform pore dimension. It allows the hydrocarbon molecule to enter the crystal based on the molecular size. Besides that, zeolite also can develop internal acidity which able to function as catalyst material. In fact, it has high ion exchange capacity and high thermal stability [2]. Therefore, zeolite is able to perform ion exchange reaction and catalyze many reactions which applied in many industrial fields.

The objective of this work is to determine the potential of natural zeolite and modified desilicated natural zeolite as base catalyst in Knoevenagel reaction. Knoevenagel reaction is used in organic synthesis to produce alkenes. Since the reaction can be catalyzed by a variety of solid bases, it could be used as probe reaction to compare basic character of different solids [3]. In this research, the natural zeolite are modified by desilication in alkaline solution and ion exchanged in order to increase the basic properties of the mordenite structure and the catalytic properties or reactivity is investigated using the modified natural zeolite. Both products obtained are characterized using a few instruments. Desilication or base leaching is a selective extraction process of silicon framework by treatment in alkaline solution. In this process, the controlled leaching of Si by OH^- form intracrystalline mesopores will facilitate the access and diffusion of molecule in zeolite [4]. It will increase the activity, selectivity and lifetime of modified zeolite in catalysis. This modification process will lead to the mesoporosity development of the zeolite structure without distinct modification

EXPERIMENTAL

Desilication with sodium hydroxide solution (NaOH)

Firstly, the solution of sodium hydroxide (3M, Qrec) was prepared by dissolving NaOH pellet (12g) with 10mL distilled water. Then, it was transferred into volumetric flask (100mL) and diluted to the mark. While, the natural zeolite (mordenite, Indonesia) was ground to obtain fine powder using mortar and pestle. Next, the powder was sieved using Laboratory testing sieve of the size 160 μm . Then, the alkaline treatment (desilication) was carried out at room temperature (RT) and 60 °C.

For reaction at room temperature natural zeolite (5g) is added into NaOH solution (100mL, 3M). Next, the mixture was shaken using orbital shaker at the speed of 160 rpm for 24hours. While for the reaction at 60 °C, the mixture of natural zeolite (5g) in NaOH solution (100mL) was stirred with an electrothermal heater using oil bath. The mixture was then separated by filtration using Hirsch funnel. The solid sample obtained was washed with distilled water and dried overnight at 100 °C. The samples were denoted as NaZ-RT and NaZ-60

Ion Exchanged process

For ion exchange process, the barium and calcium solution of 1 M was prepared by dissolving of barium nitrate, $\text{Ba}(\text{NO}_3)_2$ (26.13g, Bendosen) and calcium nitrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ (26.315g, Qrec) with 10 mL distilled water. Then, each mixture was transferred into the 100 mL volumetric flask and diluted to the mark. After that, the natural zeolite of 60°C (NaZ-60) was added into 250 mL round bottomed flask containing 100 mL prepared solution. The mixture was heated at 60 °C in an oil bath for 24 hours with stirring. Next, the product of barium and calcium exchanged natural zeolite (Ba-NaZ and Ca-NaZ) obtained were filtered with Hirsch funnel and dried in oven. The product obtained were weighed and recorded

Characterization

The modified desilicated natural zeolites and ion-exchanged desilicated natural zeolite were characterized using X-ray Diffraction (XRD, model Bruker Advance D8 diffractometer) to determine the crystallinity and phase of structure. Besides, Fourier Transform Infrared Spectroscopy (FT-IR, Perkin Elmer 1600) was used to measure the bond vibration frequencies and determine the functional group that are presence in the structure. While elemental analysis of sodium, calcium and potassium was carried out by using Atomic Absorption Spectroscopy (AAS, Perkin Elmer) to determine the single element concentration present in the zeolite sample.

Reactivity of the modified natural zeolites catalyst in Knoevenagel Reaction

The Knoevenagel reaction was carried out between benzaldehyde (0.05mol, 2.5g) with the dimethyl malonate (0.05mol, 4.0g) in the presence of catalyst. The catalyst was first activated at 500°C for 5 hour. After the catalysts added, the mixture was placed in the round bottom flask equipped with condenser. The mixture was heated in oil bath at 120 °C for 24 hours with stirring. The reaction was carried out under nitrogen gas. Then, 1 μ L of sample before and after the reaction was taken to be analyzed by gas chromatography. When the reaction complete, the product are allowed to cool down and the catalyst was separated out from the solution by filtration. In the Knoevenagel reaction, the sample taken was characterized with the gas chromatography (HP-5 column, Agilent 6890 Series). The components from the chromatogram GC obtained was identified by GC-MSD (Agilent 6890 Series)

RESULTS AND DISCUSSION

The natural zeolite, mordenite undergone modification by desilication and the ion exchange process with barium and calcium ions of alkaline earth metal. Figure 1 presents the XRD of natural zeolite NaZ and the desilicated samples.

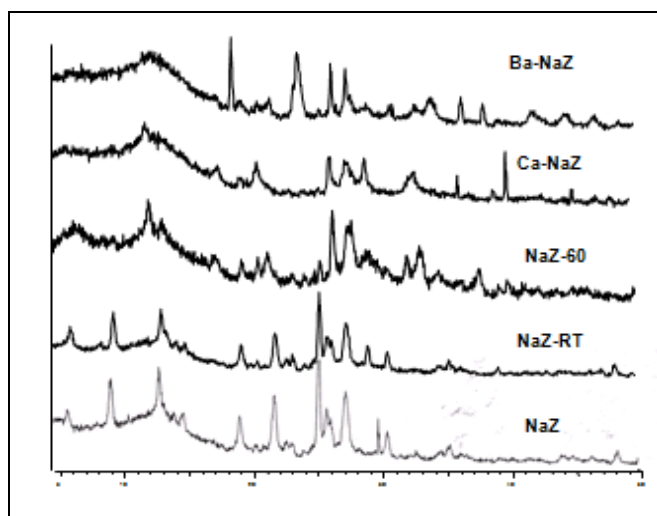


Figure 1 X-ray diffractograms of natural zeolite mordenite (NaZ) and the desilicated modified NaZ samples

From the XRD result, it was confirmed that the natural zeolite used has mordenite phase structure. From the diffractogram, it showed that for desilicated NaZ at room temperature (NaZ-RT) show similar pattern with that of NaZ. This indicates that there is no significance change to the structure. However, there a slightly change to lower intensities of the peaks after desilication under 60°C was observed. It showed the some zeolite framework structure has collapsed and preferred orientation of atom has changed. The XRD pattern of the barium ion and calcium exchanged desilicated natural zeolite (Ba-NaZ and (Ca-NaZ), shows decreased intensities the peaks and became broader, indicated that some amorphous parts started to form exist in the structure. It can be concluded that the crystallinity of the zeolite decreases from the NaZ > NaZ-RT.> NaZ-60> Ca-NaZ> Ba-NaZ.

Table 1: Percentage of crystallinity and concentration of ions in the natural zeolite and modified natural zeolite samples

Sample	% of Crystallinity	Concentration ion(ppm)				% ion exchanged
		Na ⁺	K ⁺	Ca ²⁺	Ba ²⁺	
Natural Zeolite (NaZ)	100	0.2526	0.2844	12.28	-	-
Desilicated natural Zeolite 60°C(NaZ-60)	25.39	2.171	0.1443	4.982	-	100
Calcium ion exchange Natural Zeolite(Ca-NaZ)	18.90	0.3044	0.0527	43.42	-	86
Barium ion exchange natural Zeolite (Ba-NaZ)	16.89	0.4624	0.1688	7.507	0.0020	79

The IR spectra in the Figure 2 support the XRD data. It was observed that there are no significant different between NaZ, and desilicated NaZ-RT and NaZ-60 samples in term of vibration bonding pattern. However, the asymmetric stretching bands for desilicated natural zeolite have shifted to the lower wavelength from the original natural zeolite (1046 cm⁻¹) to 1038 cm⁻¹ for NaZ-RT and 993 cm⁻¹ for NaZ-60. This indicates that the amount of framework aluminium has increased in the framework of zeolite.

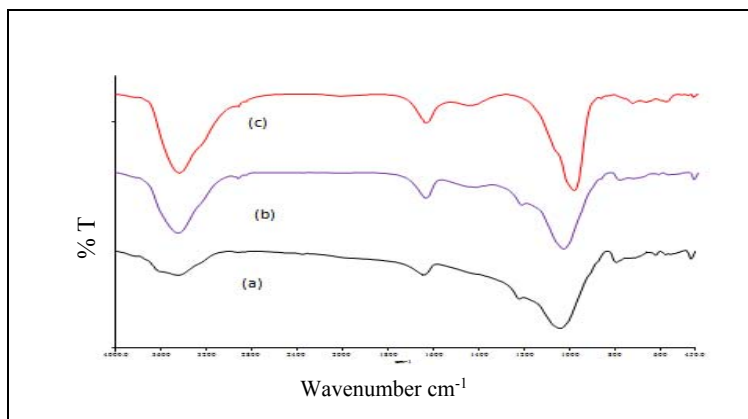


Figure 2 FT-IR spectra of (a) Natural zeolite (NaZ), (b) Desilicated natural zeolite a room temperature (NaZ-RT) and (c) Desilicated natural zeolite at 60 °C (NaZ-60)

From the elemental analysis, it can be calculated that the percentage of ion exchange of NaZ- 60 toward Ca-NaZ and Ba-NaZ are 86% and 78.7%. It showed that the ion exchanged process have been successfully be carried out by replacing sodium with barium and calcium ions.

In order to test the catalytic activity of the modified desilicated zeolite, Knoevenagel reaction had been carried out. The reaction is between benzaldehyde and dimethyl malooanate as illustrated in the equation 1 below:

Results showed that Ca-NaZ catalyst, it gave 20.8% conversion and 63.2% selectivity, while the Ba-NaZ catalyst gave 55.8% of conversion and 100 % of selectivity toward the formation of the dimethyl-2-benzylidenemalooanate (main product). It showed that the barium exchanged natural zeolite (Ba-NaZ) is active than calcium exchanged natural zeolite (Ca-NaZ) as expected since Ba has stronger basicity character than Ca based on its higher conversion. As for the selectivity, highly strength basic property facilitated for higher percentage of selectivity as was shown by the 100% selectivity obtained by Ba-NaZ catalyst.

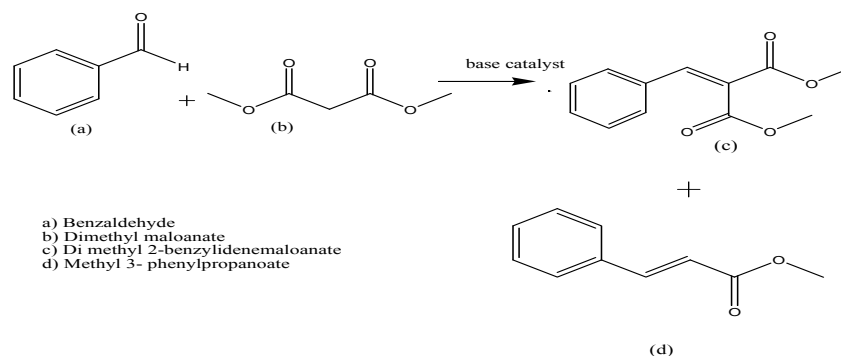


Figure 3 shows the percent conversion and selectivity for Ca-NaZ and Ba-NaZ samples. This result was obtained from analyzing the chromatogram of the liquid.

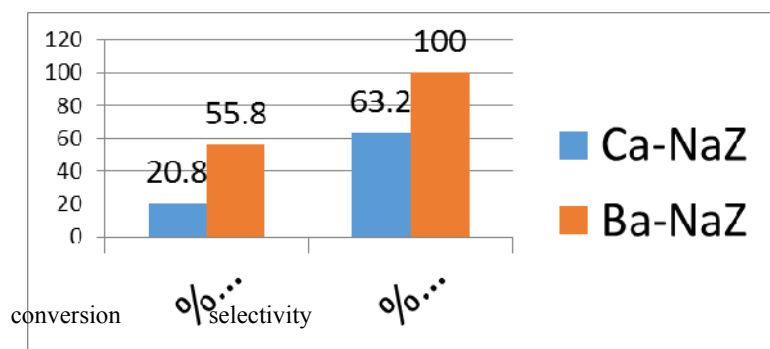


Figure 4 : Percent conversion and selectivity of Ca-NaZ and Ba-NaZ catalysts for Knoevenagel reaction between benzaldehyde and dimethyl malonate.

CONCLUSION

The modifications of the natural zeolite are successfully done by the desilication followed by ion exchanged process. Characterization on the desilicated NaZ shows the increased of Al in the zeolite framework which then enhanced the number of ions balancing the anionic zeolite framework hence increased the basicity of the ion exchanged desilicated NaZ catalysts. Reactivity of the catalysts for Knoevenagel reactions showed that the barium exchanged desilicated NaZ was more reactive than calcium exchanged desilicated NaZ with higher selectivity due the higher basicity of barium than calcium ion.

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