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Determination of Brønsted Acid Sites In Porous Aluminosilicate Solid Catalysts Using Volumetric And Potentiometric Titration Method

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Abstract. The Brønsted acid site was determined by using volumetric and potentiometric titration method. The result showed that the Brønsted acid sites of synthesized aluminosilicate using volumetric titration method are aluminosilicate-1: 0.5491; aluminosilicate-2: 0.5523; and aluminosilicate-3: 0.5772 mmol/g and using potentiometric titration method are aluminosilicate-1: 4.7087; aluminosilicate-2: 5.5739; and aluminosilicate-3: 8.1059 mmol/g. FTIR-pyridine also showed the same trend line, the Brønsted acid sites concentration increased by the increasing of Si/Al mole ratio. The results of the measurement using FTIR-pyridine showed the Brønsted acid sites concentration of aluminosilicate-1; aluminosilicate-2; and aluminosilicate-3 were 0.0293; 0.330; and 0.0336 mmol/g, respectively. The Brønsted acid sites concentration of aluminosilicate was higher using volumetric titration and potentiometric titration methods than using the FTIR-pyridine method, but the trend line was the same, the higher Si/Al mole ratio, concentration of Brønsted acid sites increased.

Keyword : Brønsted Acid, Aluminosilicate Solid, Volumetric, Potentiometric Titration

1. Introduction

The catalysts need for a wide range of organic reactions is currently increasing. The type of catalyst which is the first interest nowadays is the heterogeneous catalyst. Aluminosilicates are widely used as heterogeneous catalysts for many chemical reactions. Aluminosilicate compound can be used as a catalyst because it can react in the surface area, has a good cation-exchange capability, and its Brønsted acid properties can be used for the conversion of hydrocarbons [1, 2].

The acidity of a catalyst play an important role in catalytic properties [3]. The higher the acid site, the surface area, and the larger the pore diameter, the active site of the catalyst will be greater so that the catalytic activity will be higher [4]. The acidity of a catalyst includes the nature, amount, and strength of the acid side [5]. Various methods have been used to quantify and characterize the acidity of aluminosilicate.

Determination of Brønsted acid site can use volumetric titration method, catalyst with cation-exchange treatment, catalyst with no further purification, and also catalyst which was milled before use had the concentration of Brønsted acid sites respectively of 0.63; 0.89; and 0.39 mmol/g. Potentiometric titration method indicates a higher Brønsted acid sites concentration compared with using FTIR-pyridine method [6]. Total concentration of Brønsted acid sites on H-Beta-25; H-Beta-300; H-Ferrierite-20; and Si-MCM-48 using potentiometric titration method were 1040; 670; 1100; and 280 $\mu\text{mol/g}$, while through FTIR-pyridine method, the concentration of Brønsted acid site on H-Beta-25 acid side; H-Beta-300; H-Ferrierite-20; and Si-MCM-48 were respectively 301; 82; 357; and 12 $\mu\text{mol/g}$ [7]. Potentiometric titration could be used in matters of materials such as zeolite with micro-mesoporus pore size [8].

In a previous study, the Brønsted acid site test was performed using FTIR-pyridine [9-11]. However, the Brønsted acid site test using FTIR-pyridine was less effective as it resulted in lower acid side concentrations [7]. Therefore, in this paper, the results of the experiments from the Brønsted acid site



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test of large porous aluminosilicate catalysts synthesized from a chemical base material was done by using volumetric titration and potentiometric titration method.

2. Experimental Method

The aluminosilicate solid catalyst was inactive if used directly, so that it needed to be activated by exchanging the cations. The first step, 0.5 g of aluminosilicate solid catalyst was refluxed in 20 mL 0.5 M ammonium acetate solutions at 60 °C for 3 hours. Then, it was centrifuged on 40 rpm for 5 minutes and dried at 110 °C for 12 hours. After that, it was calcinated at 550 °C for 6 hours by heating in stages 110 °C/hour.

Determination of Brønsted acid sites which was done by using volumetric and potentiometric titration method. Determination of Brønsted acid sites was done by using volumetric titration method was done by adding 5 mL distilled water and 0.5 mL of 0.1 M NaOH solution to the 0.05 g aluminosilicate solid catalyst in Erlenmeyer flask. The suspension was stirred overnight in a close condition, then the phenolphthalein indicator was added and titrated by 0.1 M HCl solution. Titration was stopped when the solution's color changed from rose red to colorless [6].

Determination of Brønsted acid sites which was done by using potentiometric titration method was done by using glass electrode for pH measurement. 0.01 g aluminosilicate solid catalyst was suspended in 15 mL of 0.1 M NaNO₃ solution. The suspension was titrated by 0.1 M NaOH solution by stepwise addition. The distilled water, which is used to dissolve the NaNO₃, was boiled before using it. Stirring the suspension is necessary in order to achieve an effective reaction between the acid sites and the strong base [7].

3. Results and Discussion

The synthesized Aluminosilicates cannot be used as catalyst as soon as it is made. The cation on the porous site is still Na⁺ ion. The Na⁺ ion needs to be changed so that the aluminosilicate is in its acid condition. When the cation-exchange has done, the NH₄⁺ ion will attach to the porous of aluminosilicates. The reaction that happen can be seen in Figure 1.

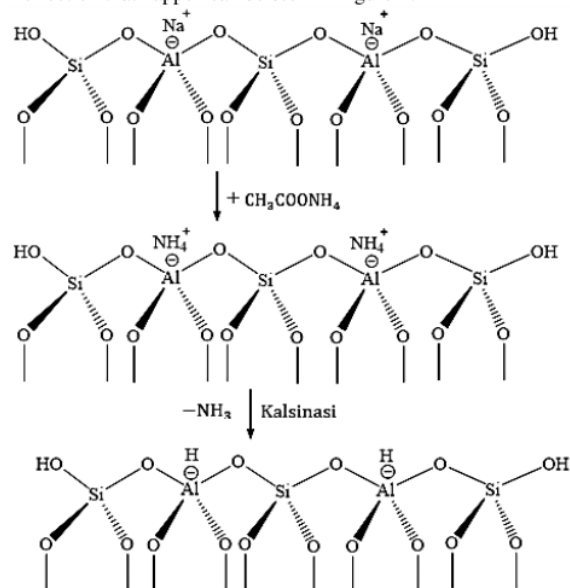


Figure 1. Cation-Exchange Reaction [12]

After the cation exchanged, the synthesized aluminosilicates solid catalyst were tested on the acid side. The results of the Brønsted acid site test using volumetric titration method showed that the Brønsted acid sites concentration of aluminosilicate-1; aluminosilicate-2; and aluminosilicate-3 were 0.5491; 0.5523; and 0.5772 mmol/g, respectively. The results of the Brønsted acid site test using potentiometric titration method showed that the Brønsted acid sites concentration of aluminosilicate-1; aluminosilicate-2; and aluminosilicate-3 were 4,7087; 5.5739; and 8.1059 mmol/g. Potentiometric graph can be seen in Figure 3. Both results show the same trend line, the higher the Si/Al mole ratio, the higher the concentration of Brønsted acid sites.

The Brønsted acid site concentration of aluminosilicate samples using FTIR-pyridine also showed the same trend line, the concentration of Brønsted acid sites increased by the increasing of Si/Al mole ratio. The results of the measurement using FTIR-pyridine showed the Brønsted acid sites concentration of aluminosilicate-1; aluminosilicate-2; and aluminosilicate-3 were 0.0293; 0.330; and 0.0336 mmol/g [13]. The Brønsted acid sites concentration of aluminosilicate samples was higher using volumetric titration and potentiometric titration methods than using the FTIR-pyridine method, but the trend line was the same, the higher Si / Al ratio, concentration of Brønsted acid sites increased [14] (can be seen in Figure 2). The concentration of acid sites of synthesized aluminosilicate with high Si/Al mole ratio can be seen in Table 1.

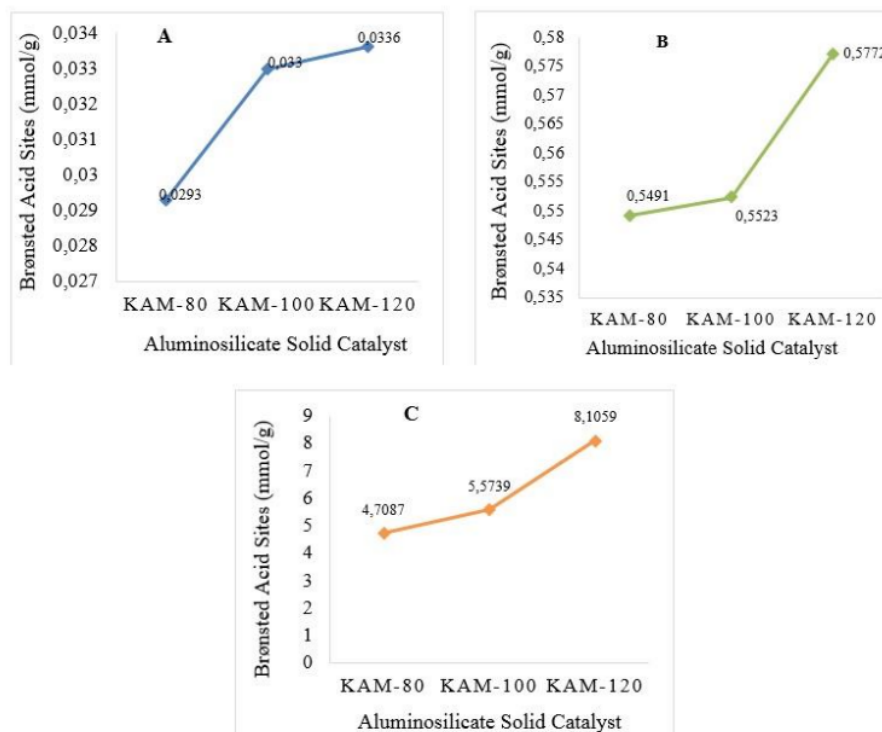


Figure 2. The Increasing of Brønsted Acid Sites Concentration of Aluminosilicate Solid Catalyst with High Si/Al Mole Ratio **A** FTIR-Pyridine Method **B** Volumetric Titration Method **C** Potentiometric Titration Method

Table 1. Concentration of Brønsted Acid Sites

Acidity Test Method	Samples	Weight (g)	Concentration of Brønsted Acid Sites (mmol/g)
FTIR-Pyridine	Aluminosilicate-1	0.0142	0.0293
	Aluminosilicate-2	0.0121	0.0330
	Aluminosilicate-3	0.0123	0.0336
Volumetric Titration	Aluminosilicate-1	0.0519	0.5491
	Aluminosilicate-2	0.0516	0.5523
	Aluminosilicate-3	0.0518	0.5772
Potentiometric Titration	Aluminosilicate-1	0.0128	4.7087
	Aluminosilicate-2	0.0115	5.5739
	Aluminosilicate-3	0.0126	8.1059

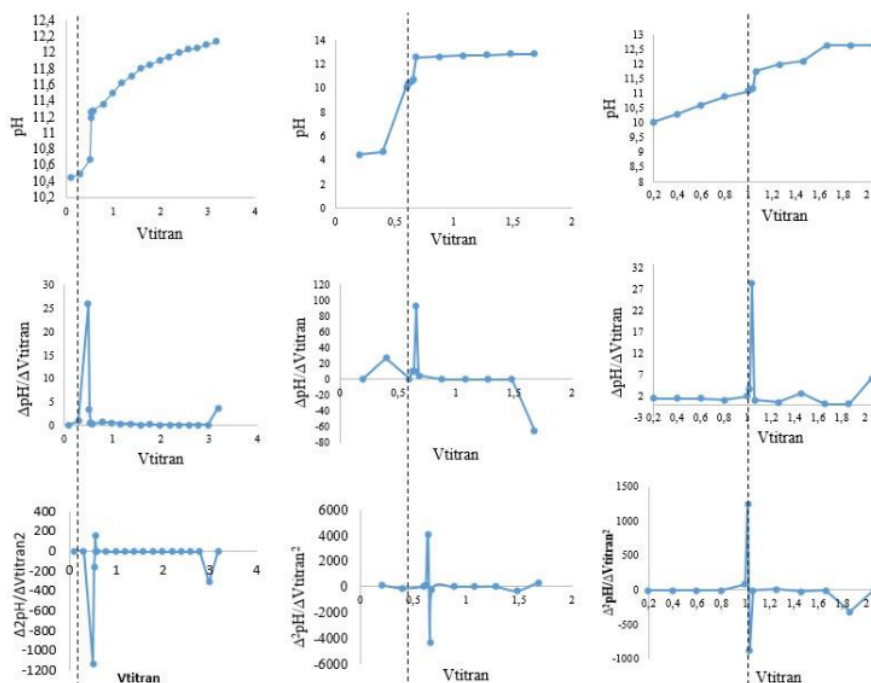


Figure 3. Potentiometric Titration Graphic (a) Aluminosilicate-1 (b) Aluminosilicate-2 (c) Aluminosilicate-3

4. Conclusions

In this study, it can be concluded that the acidity test can be done by using volumetric titration and potentiometric titration method. The results showed that the concentration of Brønsted acid sites was higher using volumetric titration and potentiometric titration method than using the FTIR-Pyridine method, with the same trend line, the higher Si/Al mole ratio, concentration of Brønsted acid sites increased.

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PAGE 2

PAGE 3

PAGE 4

PAGE 5

PAGE 6
