Surface Acidity of Sulfuric Acid Activated Maredan Clay Catalysts with Boehm Titration Method and Pyridine Adsorption-FTIR

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Abstract. The acid or base of the solid surface is a very interesting aspect at the structure of surface and important in the field of ion exchange and heterogeneous catalysts. The use of clay as a heterogeneous catalyst is due to its acidity. In this paper, the acidity of heterogeneous catalysts Maredan clay activated by sulfuric acid was examined by the Boehm titration and adsorption pyridine method. In this study, Maredan clay was activated with several variation concentration of sulfuric acid (0.5, 1, 2 and 3 M) by impregnation method. The mixture was refluxed at 80°C for 3 hours, washed with double deionised water, dried and calcined at 500 °C for 3 hours. The results showed that activation of Maredan clay by sulfuric acid produced the total acid amount of 0.6483 mmol/g catalyst by using Boehm titration method and 1.1137 mmol/g catalyst by using pyridine vapor adsorption method. FTIR analysis of the spectra of pyridine adsorption was seen that the acid site of the Maredan clay catalyst activated by sulfuric acid dominant was Lewis acid site, with wave numbers at 1449.57; 1490.07; 1573.98 and 1616.42 cm⁻¹.

1. Introduction
Surface acidity is an important characteristic in various catalytic reactions. The catalytic activity of acid solids is not only related to the surface concentration of the acid site, but also depends on the properties and strength of the acid. The acid properties of the solid surface includes the quantitative determination of acidity, the type of the acid site (Brønsted or Lewis acid) and also the reactivity of this acid center. Several methods have been used to determine the acidity of solid catalysts, i.e the Boehm titration method [1] [2], pyridine adsorption [3][4][5], and amine titration using the Hammett indicator [6][3][5][7].

Boehm titration method in determining the acidity of solids using a solution of NaHCO₃, Na₂CO₃ and NaOH. Boehm titration method divides acid groups on the surface into three categories, carboxylic acid, lactonic acid and phenolics with the assumption that NaOH neutralizes the carboxylic, phenolics, and lactonic group, Na₂CO₃ neutralizes the carboxylic and lactonic acids, and NaHCO₃ only neutralizes the carboxylic, phenolic, and lactonic acid group, so the functional group can be determined...
and calculated in number from various types of oxygenated groups [1]. The Boehm titration method has been used to determine the surface acidity of clays [8], carbons [2] and biochar [9].

Pyridine adsorption methods have also been used for the determination of surface acidity of solids such as silica-alumina [3], clay [4] [8] [10] and zeolites [5]. Pyridine is a more selective indicator for solid surface acidity because it is an aromatic Lewis base, which can act as a proton recipient from a clay surface. The acid site properties (Brønsted or Lewis acid) of the catalyst surface were determined after pyridine adsorption in the gas phase and analyzed using Fourier Transform Infra Red (FTIR). This method is very often used because the resulting absorption band can be observed in the deformation area [5], Brønsted acid sites around 1540 cm\(^{-1}\) and Lewis acid sites around 1450 cm\(^{-1}\), the total number of acid sites can be determined by Gravimetric method.

Determination of solid surface acidity using the amine titration method uses the Hammett indicator, which is based on the change in color of several indicators adsorbed on the surface of the solid that will provide a measure of acidity strength. This method is rarely applied to colored or dark samples, because the usual color changes will be difficult to observe [11].

Clay has the potential to act as a catalyst because of its acidity [12]. However, natural clay has catalytic activity and the ability of adsorption is generally not so high that it must be activated before use. Acid activation is an effective way to increase the catalytic activity of clays [13] [14]. This method involves washing clay with inorganic acid which causes the breakdown of clay particles, removal of impurities, and dissolution of the external layer, thereby changing the chemical composition and structure of the clay [14]. The use of clays in heterogeneous catalysts as solid acid catalysts is not only because of their low cost but also because the structure and dimensions of pores are more suitable for larger molecular breakdowns such as the use for esterification reactions that have been reported by Zatta, et al. (2013) [15] using phosphate activated clay, [16] [17] and [18] using sulfuric acid activated clay.

The catalytic activity and selectivity of acid-activated clay catalysts are closely related to the amount and strength of the acid sites distributed on the catalyst surface. Panda, et al. (2010) [14] was synthesis kaolinite with variation concentrations of sulfuric acid 1, 3, 5 and 10 M at 110 °C for 4 hours by reflux method and continued by calcination at 500 °C for 2 hours. The results showed that an increase in Si/Al ratio from 0.65 to 8.09 gave surface area increased from 23 to 143 m\(^2\)/g catalyst and pore volume from 0.361 to 1.18 cc/g catalyst.

According to Nurhayati et al. (2018) [18], the natural clay of Maredan village contains a type of mineral kaolinite, muscovite, and quartz. According to Hussin, et al. (2011) [19], natural clay containing kaolinite has a low specific surface area capability, low adsorption capacity and cation exchange so activation is needed to increase its catalytic properties. Activation of clay using acid is an effective way to obtain impurities that are free of impurities, increase the surface area of the catalyst and modify the structure of clay minerals [13]. Activation of clay with sulfuric acid is more widely used compared to hydrochloric acid, phosphoric acid, oxalic acid and lactic acid because of its ease of neutralization after the activation process [19]. The results of research conducted Noyan, et al. (2007) [20], that the activation of bentonite using sulfuric acid 50-60% can further increase the crystallinity, surface area, porosity and surface acidity of the catalyst.

Based on this research, this research was carried out by activating Maredan clay with varying concentrations of sulfuric acid (0.5, 1, 2 and 3 M) to determine the total acidity of the catalyst surface. The surface acidity of the catalyst was determined using the Boehm titration method and pyridine vapor adsorption analyzed by FTIR spectrum. It is expected that this research can provide information about the effect of activation of Maredan clay with sulfuric acid on the total acidity of the catalyst.

2. Methodology

2.1. Instrumentation and materials

The equipments used in this study were 100 and 200 Mesh sieves (WS Tyler Incorporated USA), three-neck flask complete with condenser, desiccator, furnace (Vulcan™ serı A-130), hotplate
magnetic stirrer (RSH-1DR), Oven (Gallenkamp), FTIR (IRPrestige-21) and other research glassware. The clay samples was from Maredan village, Tualang District, Siak Regency, Riau Province, H₂SO₄, HCl, NaOH p.a, Na₂CO₃ p.a, NaHCO₃ p.a and pyridine p.a were from Merck.

2.2. Procedure

2.2.1. Processing and activation of Maredan clay. Maredan clay sample was cleaned from their impurities and dried in an oven at 70 °C over night. Drying clay was crushed and sieved using 100 and 200 mesh. The sample used was clay which passed through 100 sieves and to be held at 200 Mesh (LM). LM chemical activation is carried out by a reflux method. A total of 25 g LM and 250 mL H₂SO₄ (variation of H₂SO₄ concentrations of 0.5, 1, 2 and 3 M) were refluxed in a three neck flask for 3 hours at a temperature of 80-85 °C. The sulfuric acid-activated clay was then washed with Aqua DM several times, then dried in an oven at 105 °C for 3 hours and continued with calcination at 500 °C for 3 hours [18], then stored in a desiccator coded LM0.5, LM1, LM2 and LM3 (LM activated with H₂SO₄ 0.5, 1, 2, and 3 M).

Determination of the surface acidity of the Maredan clay catalyst. Determination of the surface acidity of the catalyst by Boehm titration was carried out by preparing a solution of NaOH, NaHCO₃, Na₂CO₃, and HCl 0.05 N. Each of the solutions was standardized with the primary standardized solution. After standardization, 0.5 g of catalyst was immersed in 25 mL of NaOH, NaHCO₃ and Na₂CO₃ 0.05 N for 24 hours, respectively. Then each suspension was taken 5 mL of the filtrate, then titrated with 0.05 N HCl. Determination of the amount of acid on the surface of the catalyst can be calculated using Equation 1:

\[
\text{The amount of acid in the catalyst} = \frac{\left(V_B \cdot N_B - V_A \cdot N_A\right)}{W} \cdot \frac{V_p}{V_B}
\]

Where, \(V_A\) and \(N_A\) are the volumes and concentrations used from HCl as titrants, while \(V_B\) and \(N_B\) are the volumes and concentrations used from bases as titrates. \(V_p\) is the base volume during immersion, and \(W\) is the weight of the catalyst sample immersed in an alkaline solution. Determination of the number of carboxylate, lactone and phenol groups on a clay catalyst can be calculated using Equations 2 – 4:

- The amount of carboxylic acid (\(a\)) = amount of NaHCO₃ absorbed
- The amount of lactone (\(b\)) = amount of Na₂CO₃ absorbed – \(a\)
- The amount of phenol (\(c\)) = amount of NaOH absorbed – \(a\) – \(b\)

Determination of the surface acidity of the catalyst by adsorption pyridine was carried out by means of, 10 mL pyridine in a vaporizer cup placed in a desiccator to be saturated for 24 hours in a fume hood. Then in a separate place weighing the vaporizer cup to a constant and put a sample of 0.1 g. The sample in the vaporizer cup is then put into the desiccator which is saturated with the pyridine vapor. Samples were left in contact with pyridine vapor for 24 hours. After 24 hours, the desiccator is opened for 1 hour then the vaporizer cup is weighed again. Samples which had been adsorbed pyridine were directly analyzed by FTIR. Total acidity in the sample is calculated using Equation 5:

\[
\text{Total Acidity} = \frac{\left(w_1 - w_2\right)}{\left(w_2 - w_3\right) \cdot \text{BM}} \times 1000 \text{ mmol/g}
\]

where:
- \(w_1\) = Empty cup weight (g)
- \(w_2\) = Cup weight + sample (g)
- \(w_3\) = Weight of cup + sample that has adsorbed pyridine (g)
- BM = Pyridine molecular weight (79.10 g/mol)
3. Results and Discussion

3.1. Maredan clay acidity by Boehm titration method.

The results of determining the number of acid groups on the surface of Maredan clay are activated by sulfuric acid (0.5, 1, 2 and 3 M) by Boehm titration can be seen in Table 1.

Table 1. Data the result of acidity determination by Boehm titration method

| Sample   | Carboxylate (mmol/g) | Lactonate (mmol/g) | Phenolate (mmol/g) | Total Acidity (mmol/g) |
|----------|----------------------|--------------------|--------------------|-----------------------|
| LM       | 3.7081               | -0.9416            | -2.0269            | 0.7396                |
| LM0.5    | 3.7862               | -0.9409            | -2.5559            | 0.2894                |
| LM1      | 3.7817               | -1.2837            | -2.1183            | 0.3797                |
| LM2      | 3.6744               | -1.2058            | -1.8203            | 0.6483                |
| LM3      | 3.5807               | -1.0876            | -2.0179            | 0.4752                |

In Table 1, it can be seen that the surface samples of Maredan clay (LM) and Maredan clay activated by sulfuric acid (LM0.5, LM1, LM2, and LM3) only has a functional groups of carboxylic acids. On the surface of each sulfate-activated sample, the amount of the functional group of the carboxylic acid decreases with the activation treatment using H$_2$SO$_4$ at LM0.5 from 3.7862 to 3.5807 mmol/g catalyst at LM3. The reduction in the amount of carboxylates in the catalyst is due to the catalyst surface which has been activated with H$_2$SO$_4$ on the SO$_4^{2-}$ group which is the result of a reaction between clay and H$_2$SO$_4$. The S = O group that binds to clay has a relatively large molecular size which causes the absorption of NaOH, Na$_2$CO$_3$ and NaHCO$_3$ to neutralize carboxylic acid in H$_2$SO$_4$-activated Maredan clay, so that the amount of carboxylic acid in LM3 is inhibited when compared to LM0.5 which functions to neutralize carboxylic acid in H$_2$SO$_4$-activated Maredan clay, so that the amount of carboxylic acid in LM3 is inhibited when compared to LM0.5.

Panda et al. (2010) [14], has activated kaolinite clays with sulfuric acid concentrations of 1, 3, 5 and 10 M. The results obtained that activation of clays with sulfuric acid concentration of ≥ 3M can change the interlayer structure of the clay to become amorphous so that the acid groups on the clay surface increasingly reduced. Yakout, et al. (2015) [21], in his study stated that the decrease in surface area of activated carbon due to the activation treatment with H$_2$SO$_4$ because part of SO$_4^{2-}$ is located in the pore. The optimum value of total acidity of sulfate-activated samples (LM0.5, LM1, LM2 and LM3) using the Boehm titration method is found in LM2 samples which is 0.6483 mmol/g catalyst. But overall, there is no significant change in the amount of acidity with variations in sulfuric acid concentration. The amount of acid found in the clay is obtained from the number of bases that are able to neutralize the acid, but not all of the amount of the base reacts with the acid on the surface of the clay.

The XRD pattern in Maredan clay activated by 3 M sulfuric acid (LM3) [18] showed several peaks of lost kaolinite. The main peaks appear are quartz at an angle of 2θ 26.61°, 20.84° and 50.09°. Characterization of the muscovite peak can be seen from the diffraction peaks at 2θ 36.52°, 68.3° and 42.43°. The results of the analysis of the chemical composition using XRF showed that the main content of the Maredan clay catalyst activated by 3 M sulfate (LM3) was silica (SiO$_2$) at 87.05%, followed by alumina (Al$_2$O$_3$) at 11.91%. Activation of Maredan clay with 3 M sulfuric acid changed the Si/Al ratio from 1.515 to 1.741.

3.2. Acidity of Maredan clay with adsorption pyridine-FTIR

Determination of acid sites on the surface of the material is the main requirement to determine the potential for adsorption and its application as a catalyst. The results of analysis of Maredan clay (LM) and Maredan clay activated by sulfuric acid (LM0.5, LM1, LM2, and LM3) by gravimetric pyridine adsorption can be seen in Table 2 and qualitatively using the FTIR spectrum shown in Figure 1 and 2.
Table 2. Data the result of acidity determination by adsorption pyridine method

| Sample | Pyridine adsorbed (g) | Total acidity (mmol/g) |
|--------|-----------------------|------------------------|
| LM     | 0.0003                | 0.0377                 |
| LM0.5  | 0.0038                | 0.4789                 |
| LM1    | 0.0049                | 0.5991                 |
| LM2    | 0.0094                | 1.1137                 |
| LM3    | 0.0037                | 0.0929                 |

From the data in Table 2, it can be seen that the total acidity of the catalyst increased with the increase in activator concentration, i.e at LM0.5 from 0.4789 to 1.1137 mmol/g catalyst at LM2, but decreased at LM3 at 0.0929 mmol/g. LM2 has higher acidity compared to Maredan clay and sulfuric acid activated Maredan clay which is 1.1137 mmol/g catalyst.

In general, Al₂O₃ levels decrease with increasing concentrations of activators and SiO₂ content increases with these events. As research conducted by Nurhayati et al., (2018) [18] activation of clay with 3 M sulfuric acid decreased Al₂O₃ concentration to 11.906% and increased SiO₂ by 87.054%. In Panda et al. (2010) [14], in his research conducted clay activation with sulfuric acid 1, 3, 5 and 10 M which resulted in decreased Al₂O₃ levels 46.77 respectively; 42.17; 32.85; 29.38 and 7.70 % by weight. In the study, the decrease in Al₂O₃ levels due to the increase of H⁺ from sulfuric acid caused the dissolution of Al₂O₃ (dealumination) [3], it can be proved by the results of the spectrum using FTIR that the wave number shifts towards a greater direction so that the peak becomes wider (Figure 1 and 2). In Figure 1 and 2, the bands around 1637, 1549 and 1395 cm⁻¹ are considered as pyridinium ions (Brønsted acid) and 1625, 1488 and 1460 cm⁻¹ are considered as pyridine (Lewis acid). The presence of pyridine physically adsorbed on the surface by the interaction of hydrogen bonds with surface OH groups, is shown in the band around 1595 cm⁻¹ [3]. Data on the peak of the pyridine interaction spectrum in the sample can be seen in Table 3.

Figure 1. IR spectrum of adsorbed Pyridine on natural Maredan Clay (LM)
Figure 2. IR spectrum of adsorbed Pyridine on Maredan Clay activated with sulfuric acid 0.5 M (a), 1 M (b), 2 M (c) dan 3 M (d)
Table 3. The wavenumber of FTIR spectrum of pyridine interactions in the sample

| Acid site | Wave number (cm\(^{-1}\)) |
|-----------|--------------------------|
|           | LM          | LM0.5       | LM1         | LM2         | LM3         |
| Brønsted  | 1395.56    | 1394.59    | 1399.42    | 1396.49    | 1541.19    |
|           | 1488.15    | 1539.26    | 1537.33    | 1632.81    |             |
|           | 1549.87    | 1634.74    |             |             |             |
|           | 1637.64    |             |             |             |             |
| Lewis     | 1625.10    | 1456.32    | 1457.28    | 1449.57    | 1453.43    |
|           | 1490.07    | 1490.07    | 1490.07    | 1490.07    |             |
|           | 1575.91    | 1574.95    | 1573.98    | 1578.80    |             |
|           | 1616.42    | 1616.42    | 1616.42    | 1623.17    |             |
| Hydroxyl  | 1594.23    | 1596.16    |             |             | 1590.38    |

In Table 3, it can be seen that each sample has an acid site i.e Brønsted and Lewis acid sites. LM samples have the most dominant Brønsted site, whereas LM0.5, LM1, LM2 and LM3 have the dominant Lewis site. The same result was found by Ahmet and Beytullah (2001) [4], that kaolinite activated by 2 M sulfuric acid produced the nature of Lewis acid sites. Yurdakoç, et al., (1999) [3], also obtained results that Lewis acid sites that dominate in acid-activated Silica-Alumina. This is also consistent with the results of the study of Panda, et al. (2010) [14], that the acid treatment of clays with concentrations up to 3 M will be beneficial in the formation of new acid sites. When pyridine interacts with the Brønsted acid side, the pyridine molecule is protonated on the Brønsted acid side, whereas its interaction with the Lewis acid side occurs due to the formation of a complex bond of coordination between the free electron pair of the pyridine molecule and the empty orbitals of the clay surface.

Differences in the interaction of Brønsted acid in Maredan clay (LM) and Lewis acid interactions with pyridine after activated clay occurs because the activation process uses sulfuric acid (LM0.5, LM1, LM2 and LM3) can result in clay having many protons which causes Al\(_2\)O\(_3\) dissolution [14] so that dehydroxylation occurs which will form the dominant Lewis acid site.

4. Conclusion
Based on the results of research that has been conducted, it was concluded that the Maredan clay activated by sulfuric acid experienced an increase in the total amount of acidity compared to the Maredan clay without activation. The optimum total acidity was found in Maredan clay activated with 2 M sulfuric acid (LM2) of 0.6483 mmol/g catalyst analysed by Boehm titration and 1.1137 mmol/g catalyst by pyridine adsorption. Analysis using FTIR with pyridine base was found that the Maredan clay gave Brønsted acid site properties while the Maredan activated sulfuric acid clays have Lewis acid site.

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