

THE USE OF THE COMBINATION OF FTIR, PYRIDINE ADSORPTION, ^{27}Al AND ^{29}Si MAS NMR TO DETERMINE THE BRÖNSTED AND LEWIS ACIDIC SITES

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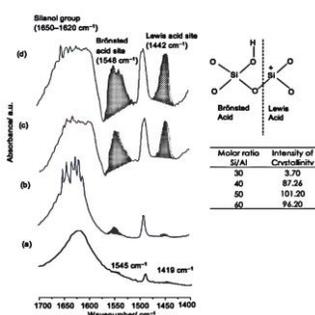
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Graphical abstract



Abstract

Lewis and Brönsted acidity were studied on ZSM-5 with combination of pyridine adsorption and FTIR vibration, ZSM-5 synthesized using kaolin Bangka Indonesia with an increase in the molar ratio of Si/Al 30-60 without pre-treatment and without organic templates and with seeds silicalite. Interestingly, the intensity of the infrared showed an increase of band vibration pyridine as absorbed Brönsted and Lewis acid sites in a molar ratio increase of Si/Al in ZSM-5, indicating an increase in the number of silanol (Brönsted acid) and deformed silica (Lewis acid) because the amount of Aluminum in ZSM-5 decrease with increase Si/Al but amount acidity increase. ^{29}Si and ^{27}Al MAS NMR analysis was supported by the results of infrared to indicate that all of the aluminum atom is coordinated with their neighbors are the same in ordering the ZSM-5 framework and ^{27}Al MAS NMR showed a sharp peak of all the variations of Si/Al except the Si/Al 30 shows a low peak area. XRD analysis supported that the ZSM-5 structure formed is pure and crystal and a decrease in crystallinity proven for more than Si/Al 50, that defects silica occurs in ZSM-5, this corresponds to the growing number of Lewis acid sites caused by defects silica described the infrared results.

Keywords: Lewis acidic sites, Brönsted acidic sites, ZSM-5, kaolin, silica defects, molar ratios Si/Al, pyridine adsorption

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1.0 INTRODUCTION

Zeolites are crystalline aluminosilicates with inner pores and cavities interconnected within channels in a defined architecture. The crystalline structure bearing a negative charge which could stabilize a whole framework by using metal ion counters species located inside the inner pore volume. These species represent active sites for acid- and redox-catalyzed reactions and they are exploited in numerous

chemical processes [1]. Besides, some other advantages have also drawn a lot of intensive investigations into zeolites since researchers have found that these materials acidic properties could offer various contributions into numerous applications [2]. For instances, zeolites can act as an absorbent in separation and purification [3-4] and they are also very useful in catalysis process [5]. It is because low aluminium content in silica-rich zeolites has resulted in specific structures and properties in their framework,

for example ZSM-5. It has been revealed that the negative charge of the AlO_4^{4-} tetrahedral is one of the decisive parameters to produce highly active topology within the zeolites framework [1,2] as it could control the Brønsted and Lewis acidic strength, the other site increase amount of aluminium could decrease strength of acidity even though increased of aluminium amount of acidity become increase [1]. Therefore, distribution of aluminium is greatly determined to come out with a controllable aluminium siting sites in T-O-T framework to enhance the chemical activities as acidity [1,16]. However, we have demonstrated an experiment which has proven that silica plays a dominant role compared to aluminium atoms to control acidity in the synthesis of ZSM-5 zeolite [6]. Indonesian Bangka kaolin as a source of aluminium content and molar ratios of Si/Al were varied to observe the effects of these compositions towards quantity of Brønsted and Lewis acidic sites in ZSM-5 by infrared, ^{27}Al and ^{29}Si MAS NMR spectroscopy. Crystallinity of the ZSM-5 zeolite was also examined in order to correlate its crystalline structure with quantity of Brønsted and Lewis acidic sites.

2.0 MATERIALS AND METHOD

2.1 Materials

All materials used in this work were analytical grade. NaOH (99 %) was purchased from Merck, Germany. LUDOX® HS-40 colloidal silica (30 % Si in water) was purchased from Aldrich, Germany. Kaolin (containing 57% SiO_2 and 22% Al_2O_3) was taken from Bangka Belitung, Indonesia. The self-synthesized silicalite and ZSM-5 were used as the seed.

2.2 Method

ZSM-5 was synthesized directly from kaolin without the organic template. The synthesis method was adopted from the experimental procedure reported previously [6]. The crystallization time used was 72 h while the molar ratios composition of zeolites were $10\text{Na}_2\text{O}:100\text{SiO}_2:2\text{Al}_2\text{O}_3:1800\text{H}_2\text{O}$.

Firstly, it was started by weighing the demineralized and deionized water, followed by dividing the weighed water into two parts. 1.00 g of NaOH was dissolved in the first half of demineralized and deionized water. Then 1.15 g of kaolin was added into it under stirring. 22.83 g of LUDOX was then added and the stirring speed was increased. After the addition of LUDOX, a homogeneous solution was formed.

Meanwhile, the second half of water was then added to the solution. The mixture was stirred at 550 rpm for 8 h. After stirring, the mixture was aged for 12 h at room temperature. 0.09 g of silicalite was added as the seed of ZSM-5. After addition of silicalite, the hydrothermal process was carried out at 175 °C as

long as 72 h [7], and this synthesis was continue for the composition ratios of Si/Al, i.e. 60, 40, and 30.

The obtained solid was washed with distilled water and dried in an oven at 110 °C for 12 h.

2.3 Characterizations

The crystal phase of the synthesized zeolite was identified using X-ray diffraction (XRD) with $\text{CuK}\alpha$ ($\lambda = 1.5405 \text{ \AA}$) radiation in 2θ from 5–40° with scanning step of 0.04°/s. The crystallinity of synthesized zeolites was calculated using equation 1 using reflection at $2\theta = 22.5\text{--}25.0^\circ$. Silicalite diffraction patterns are used as the reference.

Analysis of surface acidity were done using pyridine adsorption. A sample of 10 mg was placed on the sample holder, and put in a cell made of Pyrex glass that has a window made of calcium fluoride (CaF_2). Furthermore, the glass cell was heated at a temperature of 400 °C for 4 hours. Pyridine be absorbed at room temperature for one hour, followed by desorption at 150 °C for three hours. FTIR spectra were recorded at room temperature in the region 1700 – 1400 cm^{-1} .

Solid-state magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded on an Agilent DD2 500 MHz. The ^{29}Si spectra and ^{27}Al were recorded at resonance frequencies of 99.32 MHz with spinning rate of 9 kHz, a pulse width of 1.0 μs and a recycle delay of 5 s. The NMR spectra were deconvoluted by using a Gauss-Lorentz peak shape (Gauss/Lorentz ratio = 1:1). The integrated areas of the deconvoluted peak were used to quantify the Si/Al framework ratio using the following formula.

$$\left(\frac{\text{Si}}{\text{Al}}\right) = \frac{\sum_{n=0}^4 I_{\text{Si}(n\text{Al})}}{\sum_{n=0}^4 \frac{n}{4} [I_{\text{Si}(n\text{Al})}]} \quad (\text{equation 1})$$

where $I_{\text{Si}(n\text{Al})}$ = the total area of Si(nAl).

3.0 RESULTS AND DISCUSSION

3.1 Infrared Analysis

Infrared analysis showed three distinct vibrations as in Figure 1, which located at 1442–1419 cm^{-1} for pyridine bound coordinative with Lewis acidic site, 1548–1545 cm^{-1} for pyridine adsorbed at Brønsted acidic site [8] and 1650–1620 cm^{-1} for silanol group as acid site of Brønsted [9,10]. It is observed that these three absorption bands are increasing with the amount addition of SiO_2 . This implies that there is a correlation between types of ZSM-5 framework lattice vibrations (band wavenumber) with a series of Si/Al molar ratios.

Infrared analysis displayed that an increase of the vibration absorption bands of pyridine adsorbed Brønsted and Lewis acidic sites when molar ratios of Si/Al were increased, which indicating the increasing amount of silanol groups (Brønsted acid) and silica

defects (Lewis acid). The peak intensities of molar ratios Si/Al 50 and 60 (Figures 1c–d) have increased tremendously compared to molar ratios Si/Al 30 and 40 (Figures 1a–b). Interestingly, the absorption bands of Brönsted and Lewis acidic sites also become broader with increasing of molar ratios Si/Al. This might be due to combination of several vibrations in the framework, including electron deficiency from silicon oxide and aluminium oxide species occur at $1442\text{--}1419\text{ cm}^{-1}$ (Lewis acidity), meanwhile, there are also resulted from distinctive defects of hydroxyl groups present at $1548\text{--}1545\text{ cm}^{-1}$ (Brönsted acidity) [8] and this has also affected the neighboring silanol groups at $1650\text{--}1620\text{ cm}^{-1}$ (Brönsted acidity) [9,10].

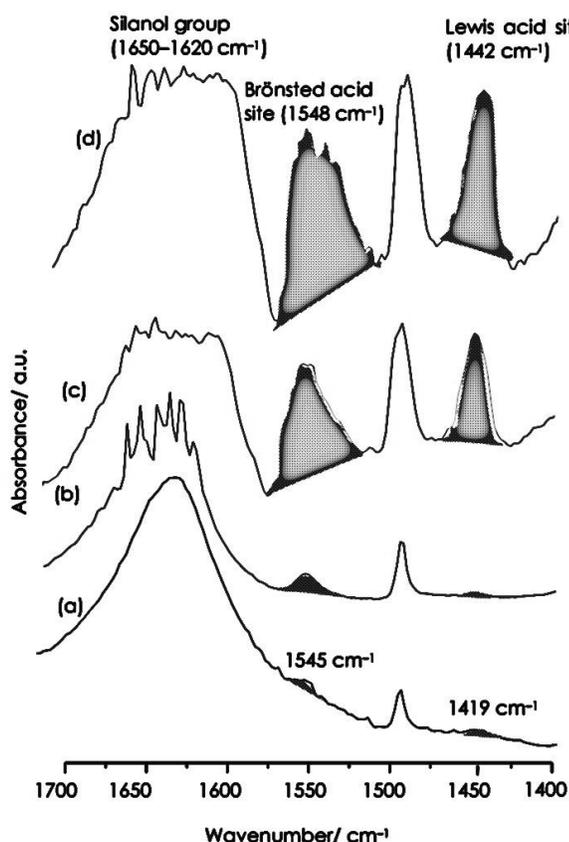


Figure 1 FTIR spectra of pyridine adsorbed on ZSM-5 zeolite containing a series of Si/Al molar ratios with (a) Si/Al 30, (b) Si/Al 40, (c) Si/Al 50 and (d) Si/Al 60

The silanol group's vibration might consist of four types functional groups (11, 12, 13): (i) isolated, non-hydrogen bonded (SiOH) as free and geminal groups; (ii) hydrogen bonded silanols as vicinal group (hydrogen perturbed); (iii) terminal hydrogen bonded silanol (oxygen perturbed); (iv) intraglobular silanols indicating weak particle interaction. The broad absorption band at $1650\text{--}1620\text{ cm}^{-1}$ was attributed to overlapping of bending absorptions from water (H-O-H) and aluminium hydroxide (Al-OH) groups. However, it is impossible for these peak

intensities to further increase as the defects have caused reducing number of hydroxyl groups and also, limited amount of aluminium content from kaolin to form Al-OH and Si-OH in the ZSM-5 framework. The same trend happened to molar ratios Si/Al 50 and 60 for Lewis and Brönsted acidic sites, showing also slightly increase in the peak intensities.

Since FTIR spectroscopy demonstrated that aluminium is not a dominant in acidity for this research. Since this spectroscopy could not prove the quantity of silicon and substitution of aluminium content in framework or extraframework, thus ^{29}Si and ^{27}Al MAS NMR were adopted as a complementary information for infrared analysis.

3.2 ^{27}Al MAS NMR Analysis

^{27}Al MAS NMR spectroscopy is used to determine the coordination number of aluminum atoms in the ZSM-5 and is used to identify whether there are species extraframework aluminum oxide, so that can know the role of the aluminum surface acidity.

Figure 2 shows that the peak signal is low and wide to the molar ratio Si/Al 30 (Figure 2a), this ratio has varied coordination and not within the framework of ZSM-5 (Figure 2b-d). Meanwhile a sharp peak at the molar ratio of Si/Al of 40 to 60. It shows the aluminum atoms have been coordinated with neatly within the frame ZSM-5.

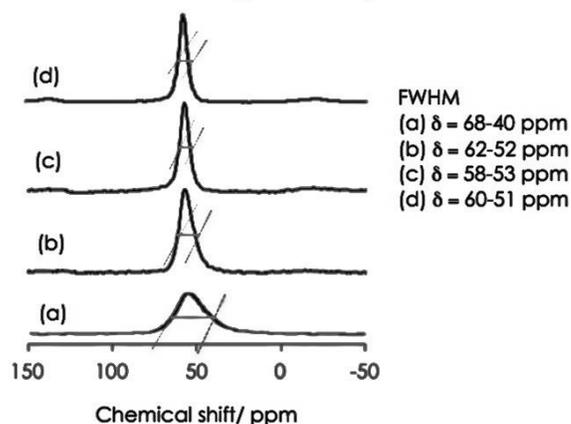


Figure 2 The ^{27}Al MAS NMR spectra of ZSM-5 zeolite containing a series of molar ratios with (a) Si/Al 30, (b) Si/Al 40, (c) Si/Al 50 and (d) Si/Al 60

^{27}Al NMR also confirmed that the absence of aluminum oxide species in extraframework around δ 25 and 13 to -17 ppm for the molar ratio of Si/Al 40 – 60. Furthermore, the shift in the chemical aluminum look very neat and sharp around and above 50 ppm (it is 60 ppm for this study), showed aluminum atoms tetrahedrally coordinated to neighboring species within the framework of ZSM-5 [14]. Aluminum is contributing properties of surface acidity as acid Brönsted, as a result of the entire aluminum in ZSM-5, but the increase in the mole ratio of Si/Al in the

framework of ZSM-5, should be to lower the acid content of Brönsted, but with increasing Si/Al actually increase the acidity of Brönsted. Therefore, the increase in acidity is not due to the amount of aluminum in the ZSM-5, but there are other factors .

3.3 ^{29}Si MAS NMR Analysis

The results from ^{29}Si solid state MAS NMR are very strongly correlated with the ^{27}Al MAS NMR spectra. The local environment of silicon and its heteroatom, *i.e.* aluminium content substituted in the ZSM-5 framework, were examined by ^{29}Si solid state MAS NMR. It is seen that ZSM-5 zeolite consisted of two main peaks, which are denoted as $\text{Q}^3=\text{HOSi}(\text{OSi})_3$ (δ 97 ppm) and $\text{Q}^4=\text{Si}(\text{OSi})_4$ (δ 107 ppm) as shown in Figure 3.

Typically, the $\text{Q}^4=\text{Si}(\text{OSi})_4$ and $\text{Q}^3=\text{HOSi}(\text{OSi})_3$ are located at chemical shift of δ 110 and δ 100 ppm [11]. However, Figure 3 illustrates that ^{29}Si resonance at lower chemical shift (\sim 10 ppm), which is due to the substitution from aluminium content into the siliceous framework [14,15]. The Q^3 and Q^4 peaks were not well-resolve (Figure 3a) when molar ratio of Si/Al with 30 was added into the mixture solution containing kaolin, NaOH, water, and silicalite seed. It is due to the presence of aluminium amount is nearly equal to silicon concentration, whereby aluminium and silicon concentrations are proportional to the intensities of all the resonances, represented by these environments $\text{Si}(\text{OSi})_{4-x}(\text{OAl})_x$ [15].

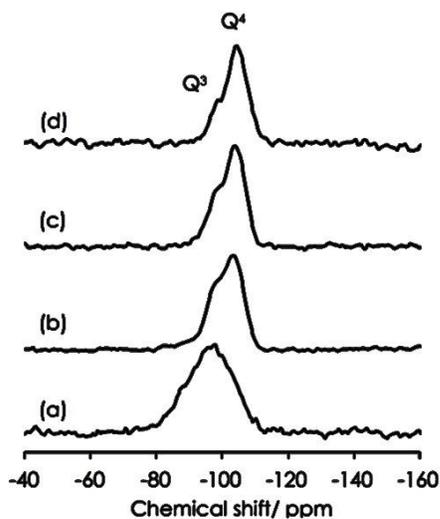


Figure 3 The ^{29}Si solid state MAS NMR spectra of ZSM-5 zeolite containing a series of molar ratios with (a) Si/Al 30, (b) Si/Al 40, (c) Si/Al 50 and (d) Si/Al 60

There is another worth noting information in Figure 3a, in which the spectrum is broader compared to Figures 3b–d because involvement larger amount of aluminium from kaolin but lower silicon concentration

from silicalite, has caused local disorder in the lattice of ZSM-5 framework substitution [15,16].

It is observed that Q^3 and Q^4 peaks were well-resolve with an increase for the amount of SiO_2 (molar ratios of Si/Al from 40 to 60). This evidence stated that the silicon coordinates in ordered way with its neighboring $-\text{OSi}$ or $-\text{OAl}$ groups. In contrast, the Q^3 peak intensities decreased (Figures 3b–d) with higher amount of SiO_2 added, which indicating that the concentration of $\text{Q}^3=\text{HO-Si}(\text{OSi})_3$ and $\text{AlO-Si}(\text{OSi})_3$ were reduced and more $\text{Q}^4=\text{Si}(\text{OSi})_4$ signals were formed with gradual chemical shift to right [1,16].

Despite of the reduced peaks of Q^3 (Figures 3b–d) seem to be contradictory with the infrared spectra which showed the almost similar peak intensities of silanol groups (Figures 1b–d), this infrared analysis' trend is due to overlapping of the water with the silanol groups, whereas ^{29}Si solid state MAS NMR can accurately detect the local structure of silicon atoms.

Since Q^3 can be assigned to either $\text{HO-Si}(\text{OSi})_3$ or $\text{AlO-Si}(\text{OSi})_3$ which are overlapping in the same region, therefore ^{27}Al MAS NMR was used to identify the aluminium species as illustrated in Figure 2.

3.4 XRD Patterns Analysis

Figure 4 shows the XRD patterns of (a) kaolin and ZSM-5 zeolite framework added with a variation of molar ratios of (b) Si/Al 30, (c) Si/Al 40, (c) Si/Al 50 and (d) Si/Al 60. These data are very significant in proving that the local coordination of silicon and aluminium are in a pure and crystalline ZSM-5 structure.

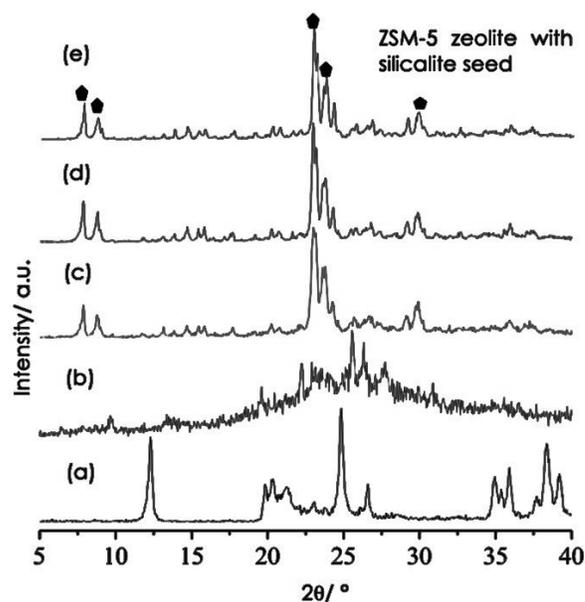


Figure 4 XRD patterns of ZSM-5 zeolites for the (a) kaolin, molar ratios of (b) Si/Al 30, (c) Si/Al 40, (c) Si/Al 50 and (d) Si/Al 60

XRD pattern of kaolin was included in Figure 4 as a comparison result to show structure of kaolin was disappeared to form ZSM-5 after some treatments, and also the increase of molar ratios Si/Al have no more contained the kaolin structure. It is clearly seen that the XRD pattern of molar ratio Si/Al 30 was broad without any apparent sharp peak, indicating it is in bulk, unorganized arrangement or amorphous structure. It is in agreement with ^{27}Al and ^{29}Si NMR results which were broad peaks and their resonances at slightly higher chemical shifts. Conversely, Figures 4c-e show an increase in the peak intensity with higher molar ratio of Si/Al (40-50) added, indicating the crystallinity of ZSM-5 has increased gradually. This is consistent with the sharp peaks of ^{27}Al and ^{29}Si NMR spectra, showing the arrangements neat or coordinative bonds (high crystallinity) as in XDR pattern. This corresponded to a method and materials synthesis where the current seed Si/ higher need for resetting the synthesis parameters in order to get a good crystallinity.

Table 1 The correlation between intensity of crystallinity with molar ratios Si/Al from 30 to 60

Molar ratio of Si/Al	Intensity of Crystallinity
30	3.70
40	87.26
50	101.20
60	96.20

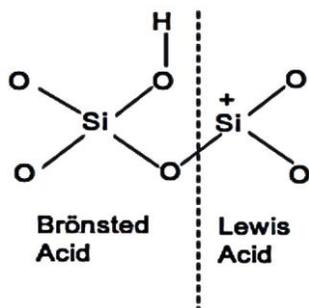


Figure 5 Site defect which have 2 site active

However, Table 1 shows a decrease in crystallinity in the molar ratio of Si/Al 60, the decline was due to the crystallinity of the content of some of the crystal defects on silica ZSM-5 framework. Where a series of Si-O-Si were happen to occur interglobular silanol very weak so that the interruption of the bond to form Si-OH sites as silanol (Bronsted acid) and sites Si^+ as a Lewis acid sites. so this is what causes the decline in the content of Al (or Si/Al increase) but increased the number of Brønsted and Lewis acidity simultaneously. This fact correlates with the data FTIR

(Figure 1) and the XRD data that form the crystallinity of ZSM-5 (Table 1) consists of defects in Brønsted and Lewis broad band on the molar ratio of Si/Al 60.

4.0 CONCLUSION

The use of the combination FTIR-pyridine adsorption, XRD analysis, ^{27}Al and ^{29}Si MAS NMR in determining the distribution of Al and Si has been demonstrated in this research. It has been shown that the molar ratios of Si/Al are the determining factor for the Brønsted and Lewis acidities of the ZSM-5 surface. Increasing of the Brønsted acidic sites are due to the presence of silanol groups while increasing of the Lewis acidic sites are owing to several silica defects. ^{29}Si and ^{27}Al MAS NMR analyses have proven that aluminium atoms are coordinated with their neighbours in ordered framework after molar ratios of Si/Al 30. XRD analysis has also supported that the structure formed is pure and crystalline ZSM-5, but its crystallinity decreased at molar ratio Si/Al 60 which confirmed that the structure consists of some defects. Lastly, we conclude that, based on the results, Brønsted and Lewis acidities of the ZSM-5 are affected by the Si/Al molar ratios with silanol and silica as the dominant factors, instead of the typical research findings that the aluminium component plays a main role in acidity.

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