

Article

Aluminosilicates Catalysts Synthesis from Low-Grade Indonesian Kaolin for the Acetalization Reaction

Hartati Hartati ^{1,*}, Qurrota A'yuni ¹, Nastiti Heru Saputri ¹, Dea Zaqiatul Mardho ¹, Putri Bintang Dea Firda ¹, Hartono Hartono ², Hasliza Bahruji ³, Reva Edra Nugraha ⁴, Novia Amalia Sholeha ⁵ and Didik Prasetyoko ^{6,*}

¹ Department of Chemistry, Faculty of Science and Technology, Universitas Airlangga, Campus C UNAIR, Mulyorejo, Surabaya 60115, Indonesia

² Department of Mining Engineering, Faculty of Mineral Technology, University of Pembangunan Nasional "Veteran" Yogyakarta, Yogyakarta 55283, Indonesia

³ Centre for Advanced Material and Energy Sciences, Universiti Brunei Darussalam, Jl. Tungku Link, Gadong BE1410, Brunei

⁴ Department of Chemical Engineering, Faculty of Engineering, Universitas Pembangunan Nasional "Veteran" Jawa Timur, Surabaya 60294, Indonesia

⁵ College of Vocational Studies, Bogor Agricultural University (IPB University), Jalan Kumbang No. 14, Bogor 16151, Indonesia

⁶ Department of Chemistry, Faculty of Science and Data Analytics, Institut Teknologi Sepuluh Nopember (ITS), Surabaya 60111, Indonesia

* Correspondence: hartati@fst.unair.ac.id (H.H.); didikp@chem.its.ac.id (D.P.)

Abstract: Aluminosilicate and ZSM-5 catalyst were synthesized from local materials, low-grade Indonesian kaolin. High quartz impurities content in the low-grade kaolin was successfully reduced by the consecutive treatment process including washing, centrifugation, and Fe³⁺ treatment. All the synthesized catalyst showed mesoporous structure with pore diameter around 3.5 nm. The catalytic activity was investigated in the acetalization of 3,4-dimethoxybenzaldehyde and propylene glycol, then the effect of a different base (TPAOH and NaOH) and Fe³⁺ addition in the treatment process to the catalytic activity was discussed. The catalytic activity of the aluminosilicate catalyst outperforms the ZSM-5. Interestingly, it is found that the catalytic activity of the catalyst can be enhanced by addition of Fe³⁺ in the aluminosilicate, with enhanced the conversion from 32.2% to 81.6%, whereas Fe³⁺ addition to ZSM-5 showed slightly increased conversion value from 0% to 3.65%. All catalysts showed high selectivity of 100% of the reaction product 2-(3,4-dimethoxy-phenyl)-4-methyl-1,3-dioxolane.

Keywords: aluminosilicate; local materials; kaolin; Fe³⁺; ZSM-5; acetalization



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1. Introduction

Perfumery chemicals are essential ingredients in personal care and household products, with the current market estimated to reach two billion USD in 2024 [1]. The development of synthetic fragrances via homogenous or heterogenous reactions offers a feasible method to reduce the cost of extracting fragrances from plants, herbs, and animals [2]. The transition from homogeneous catalyst to heterogeneous reaction enhanced the stability and reusability of catalysts while preventing harmful reagents [3]. Acetalization is a widely investigated reaction for synthesizing fragrance ingredients from the reaction between aldehyde and alcohol to form acetal molecules [4,5]. Acetalization requires either homogenous acid catalysts [6] such as sulfuric acid, NCS (N-chlorosuccinimide)/thiourea, and sulfonic acid; or heterogeneous solid acid catalysts such as zeolite, HPA (heteropoly acid), and aluminosilicates [7–9]. Homogeneous catalyst has undeniable disadvantages, particularly the lack of reusability, the tedious product separation, and toxic waste by-product. A heterogeneous solid acid catalyst is ideal for overcoming these problems [10]. Aluminosilicate and ZSM-5 have been investigated as catalysts for acetalization due to their adjustable acidity, porosity,

and particle size [2,11]. The activity of zeolite is strongly dependent on the acidity, porosity, and particle size. Catalysts with mesoporosity enhanced the diffusion. Meanwhile, small particle size increased the surface area of catalysts [12]. Therefore, these three parameters are often modified to increase performance [13,14].

In this study, the potential of low-grade kaolin as silica and alumina sources is used to synthesize aluminosilicate and ZSM-5. Low quality kaolin is indicated by the relatively low kaolinite content and the presence of impurities such as quartz, calcite, and iron oxide. The synthesis parameters are optimized with the variation of base concentration, NaOH and TPAOH (sodium hydroxide and tetrapropylammonium hydroxide), and hydrothermal condition (time and temperature). Textural properties of the catalysts are determined using XRD (X-ray diffraction), FTIR (Fourier transform infrared), SEM-EDX (scanning electron microscope energy dispersive X-ray), and N_2 adsorption–desorption analysis. Finally, the activity of the catalyst and the effect of Fe^{3+} loading are determined for the acetalization of 3,4-dimethoxybenzaldehyde and propylene glycol.

2. Results and Discussion

2.1. Characterisation of Kaolin and Catalysts

X-ray diffraction pattern of raw kaolin showed the presence of a very intense peak associated with quartz at 26.6° . The XRD pattern of kaolin before and after treatment (washing and centrifugation) in Figure 1 showed that the intensity of quartz peak at 26.6° decreased significantly. However, the peaks corresponding to kaolin were still visible without significant intensity changes in line with XRF data (Table 1). XRF analysis exhibited that the SiO_2 content was decreased from 69.4% to 58.1%. This result suggested that through repeated washing and centrifugation, the kaolin has separated quartz from kaolinite, due to the higher density of quartz. Quartz is unreactive when treated with water but dissolves into colloidal silica and silicic acid. Quartz dissolution is enhanced by increasing the pH. The presence of alkaline oxides such as Ba_2O and K_2O as impurities in kaolin was suggested to create a basic environment to promote the dissolution of quartz [15,16].

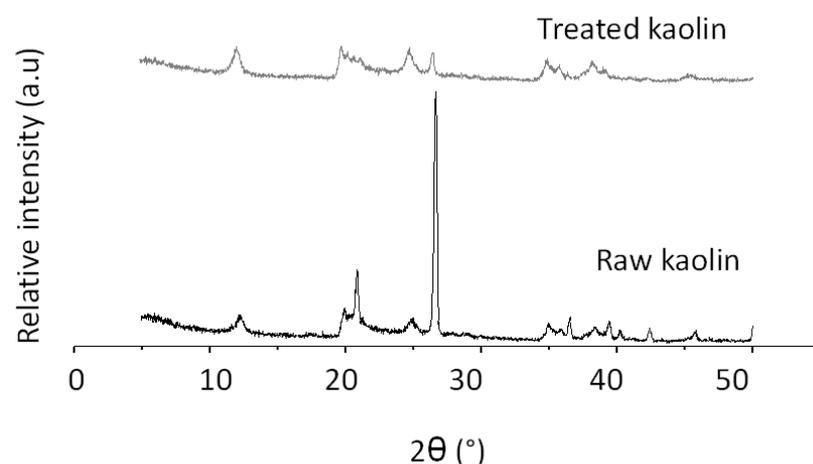


Figure 1. XRD pattern of raw kaolin and treated kaolin.

The XRD pattern of aluminosilicate when synthesized using NaOH and TPAOH as templates is shown in Figure 2. When NaOH was used as a template (Figure 2a), the peaks associated with AN at 19.5° and 26.54° were only observed on the sample following hydrothermal synthesis at 24 h. AN-1 obtained at 12 h and then 24 h did not show any crystalline peak, while AT-1 (Figure 2b) showed peaks at 8.69° , 19.62° , 23.14° , and 26.54° . In contrast to AN-1, AT-1 shows a hump at around $20\text{--}30^\circ$ indicating the presence of an amorphous phase in the sample. The peak at 26.6° is the characteristic of a quartz peak, while the peak at 19° is moganite [17]. This result indicates that the aluminosilicate was started to form. AN-2 showed an irregular pattern, while AT-2 showed the early growth of ZSM-5 peak at 8.11° , 8.89° , 21.03° , 23.23° , 24.08° , 24.58° , 29.41° , 30.07° . AN-3 and AN-4

showed a similar pattern with the amorphous broad peak at 20–30° with quartz peak at 26.6°. Based on the successful transformation into a high crystalline aluminosilicate framework, samples synthesized with NaOH, AN-4 synthesized using NaOH will be used for catalytic testing.

Table 1. Variations in composition of the Indonesian kaolin before and after treatment.

Compound	Composition (%b/b)	
	Raw Kaolin	Treated Kaolin
Al ₂ O ₃	22.0	32.5
SiO ₂	69.4	58.1
K ₂ O	0.86	2.53
CaO	2.34	0.58
TiO ₂	1.28	1.21
V ₂ O ₅	0.02	0.03
Cr ₂ O ₃	0.13	0.03
MnO	3.1	0.15
Fe ₂ O ₃	0.08	4.39
CuO	0.51	0.06
ZnO	0.06	0.06
BaO	0.15	0.08

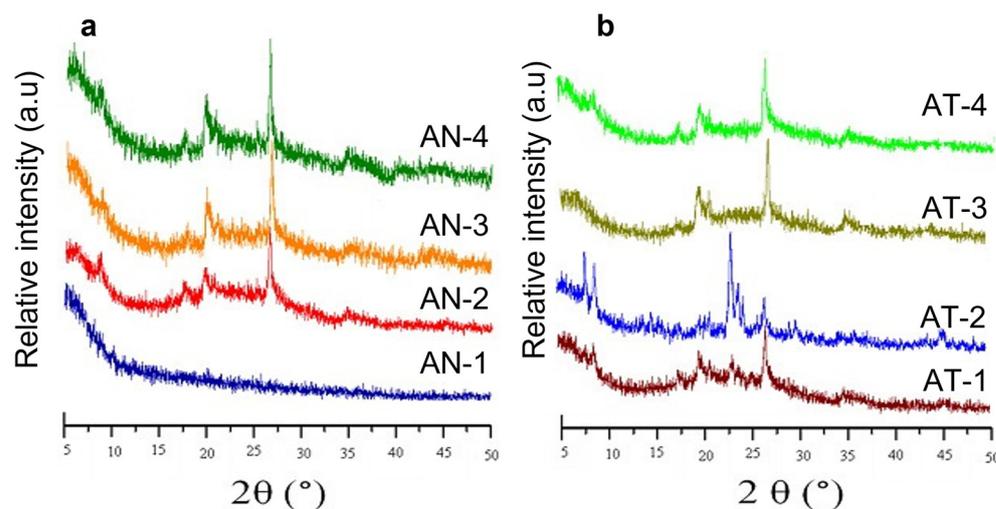


Figure 2. XRD pattern of aluminosilicate synthesized using NaOH (a) and TPAOH (b) as template.

Apart from synthesizing aluminosilicate from kaolin, ZSM-5 was also synthesized using NaOH and TPAOH. Figure 3a showed the ZSM-5 synthesized using NaOH; meanwhile, Figure 3b showed the XRD peaks of ZSM-5 obtained using TPAOH. ZT-1 and ZT-2 showed a similar pattern with ZT-3, with the formation of characteristic peaks of ZSM-5 at 8°, 8.8°, 13.9°, and 24.4° with low intensity. Moreover, quartz peaks at 26.6° and kaolin peaks at 20.9° were also observed. ZN-2 and ZN-3 showed a similar pattern to the previous diffractogram, but there is no ZSM-5 peak at 24.4. In contrast, ZT-3 showed more ZSM-5 peaks with higher intensity. Moreover, there are no peaks assigned to kaolinite and quartz. The result indicates that as the reaction time increased, kaolinite was transformed into pure ZSM-5 at 96 h. ZT-3 (synthesized with TPAOH) has the best crystallinity compared to other samples.

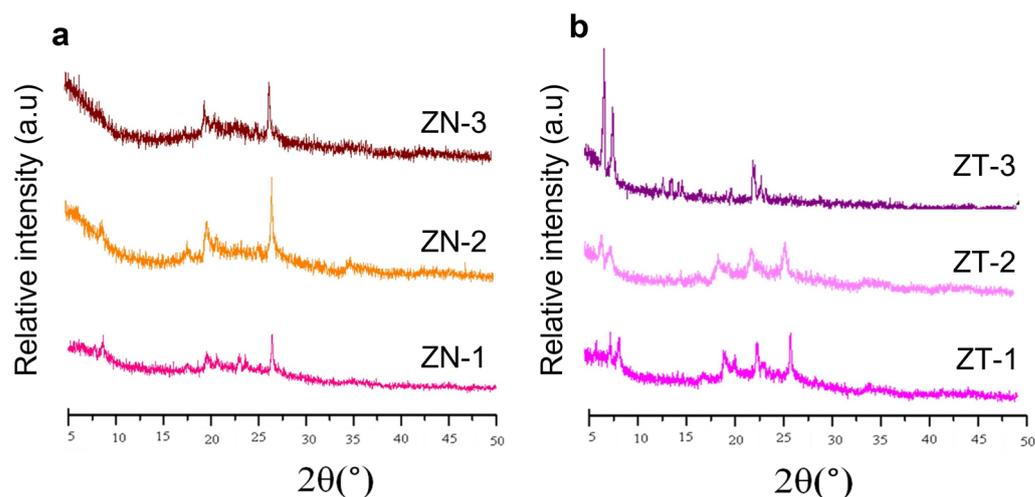


Figure 3. XRD analysis of ZSM-5 synthesized using NaOH (a) and TPAOH (b) as template.

FTIR spectra of the aluminosilicate were shown in Figure 4 and the ZSM-5 in Figure 5. The vibrational band of Si-O-Si and Si-O-Al were appeared at 1019, 1040, and 1118 cm^{-1} [18]. A characteristic band of silica showed at wavenumber between 480–800 cm^{-1} . Meanwhile, the characteristic band of five-membered ring MFI structure on the sample AT-2 appeared at a wavenumber between 550–560 cm^{-1} [19]. Synthesized zeolite spectra showed similar pattern. Bending vibration of T-O showed as band at 450 cm^{-1} . The characteristic of the MFI structure band showed at 547 cm^{-1} . The symmetric stretching band of Al-O internal tetrahedral TO_4 showed at 650 cm^{-1} , while the external stretching showed at 800 cm^{-1} . The external symmetric stretching band of Si-O-T showed at 1080 cm^{-1} , while the asymmetric stretching band showed at 1230 cm^{-1} . The presence of the MFI structure characteristic band indicates the formation of ZSM-5 framework [19].

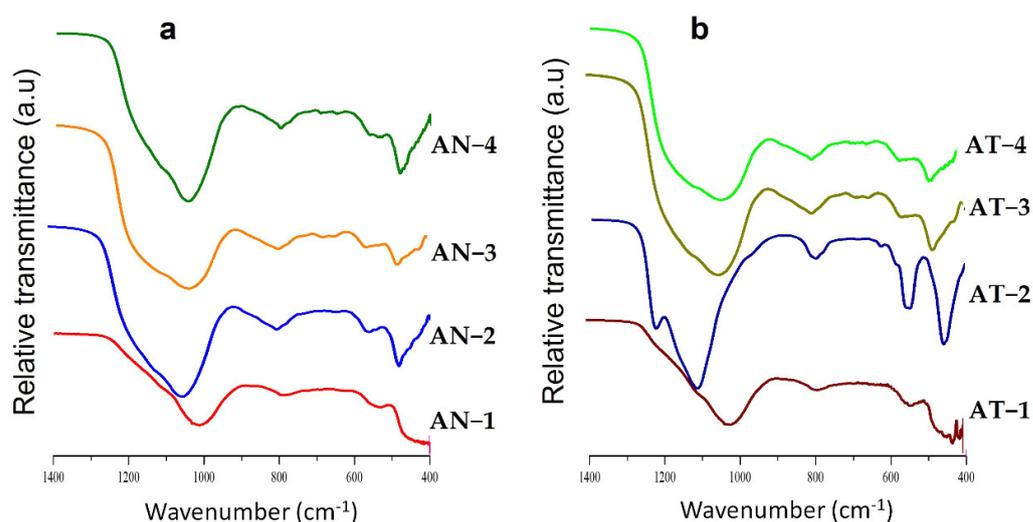


Figure 4. FTIR spectra of aluminosilicate synthesized using NaOH (a) and TPAOH (b).

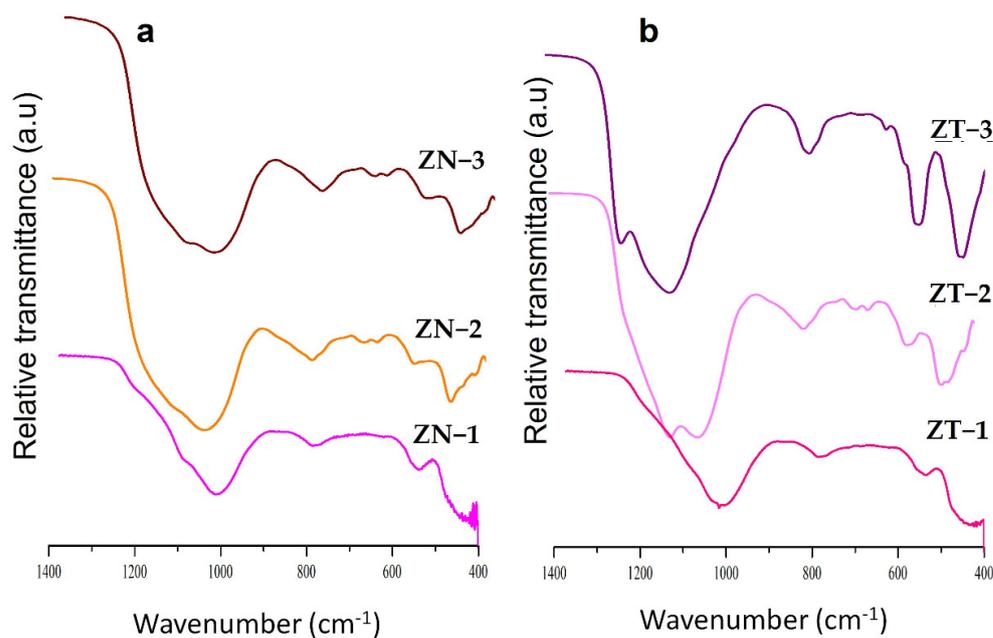


Figure 5. FTIR spectra of ZSM-5 synthesized using NaOH (a) and TPAOH (b).

Figure 6 showed the XRD pattern of the aluminosilicate AN-4 and ZT-3 following with the Fe addition. The peak around 20° with low intensity is one of the ZSM-5 characteristic peaks. Quartz peak showed at 26.6°. In contrast, ZT-3 showed the characteristic of ZSM-5 peaks with significantly higher intensity.

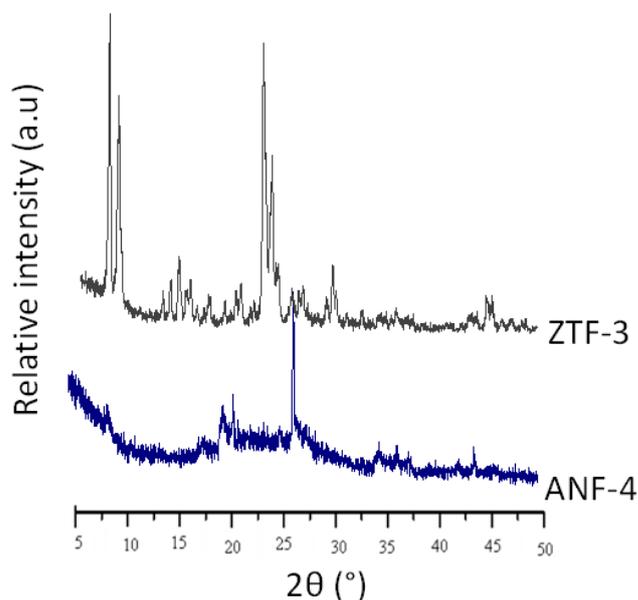


Figure 6. XRD pattern of aluminosilicates and ZSM-5 impregnated by Fe³⁺.

Figure 7 showed the SEM image of the aluminosilicate catalyst before and after Fe³⁺ addition. The images showed diverse morphological shapes and particle sizes. The particle size analysis showed that AN-4 has particle sizes 3.07 μm. This result indicates that the synthesized aluminosilicate is not in the form of nanoparticles. This might be related to the hydrothermal temperature that is not high enough to form nanoparticles [20]. The particles with irregular shapes indicate the presence of material with an amorphous phase. In comparison, round-shaped and cubic-shaped particles indicate the presence of crystalline materials.

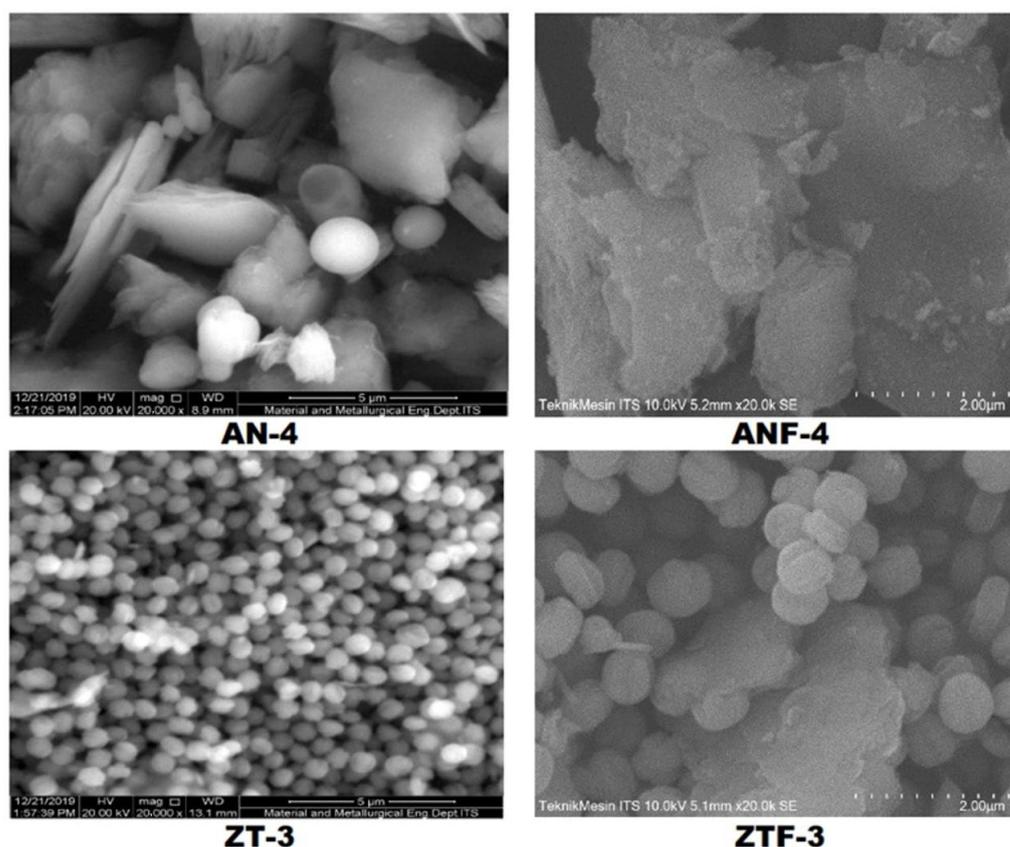


Figure 7. SEM images of aluminosilicates and ZSM-5 before and after Fe^{3+} addition.

The presence of amorphous materials can be indicated as aluminosilicate, while the presence of crystalline materials might be from quartz, iron metal, or other impurities [21]. The SEM image of both impregnated aluminosilicates showed irregular shape and morphology. The Fe^{3+} content of impregnated aluminosilicate analysed by EDS mapping (Figure 8) showed that ANF-4 has 4% of Fe. The shape morphology of ZTF-3 is also depicted in Figure 7. ZTF-3 showed ZSM-5 particles with mostly similar hexagonal shape and size. The particle size analysis showed that ZTF-3 has particle size 1051–1192 nm. This result indicates that the sample is not a nanoparticle. The composition analysis result showed that ZTF-3 has 2% Fe content (Figure 8).

Further analysis was conducted to determine the textural properties of the catalyst i.e., pore distribution, pore volume, and surface area (Figure 9). All the samples exhibited the IV isotherm as the characteristic of mesoporous materials. For the pore size distribution, all samples showed the presence of a high peak in the range < 2 nm (micropore) and smaller peaks in the range of 2–8 nm (mesopore). The textural properties of the catalysts were summarized in Table 2. The aluminosilicate catalyst synthesized with NaOH have higher surface and total pore volume, than ZSM-5 catalyst due to the fact that NaOH as alkali hydroxide is a stronger base than TPAOH as organic base [22]. The stronger base as demineralizing agent will alter the dissolution of the silica or alumina faster to induce zeolite crystal growth [23].

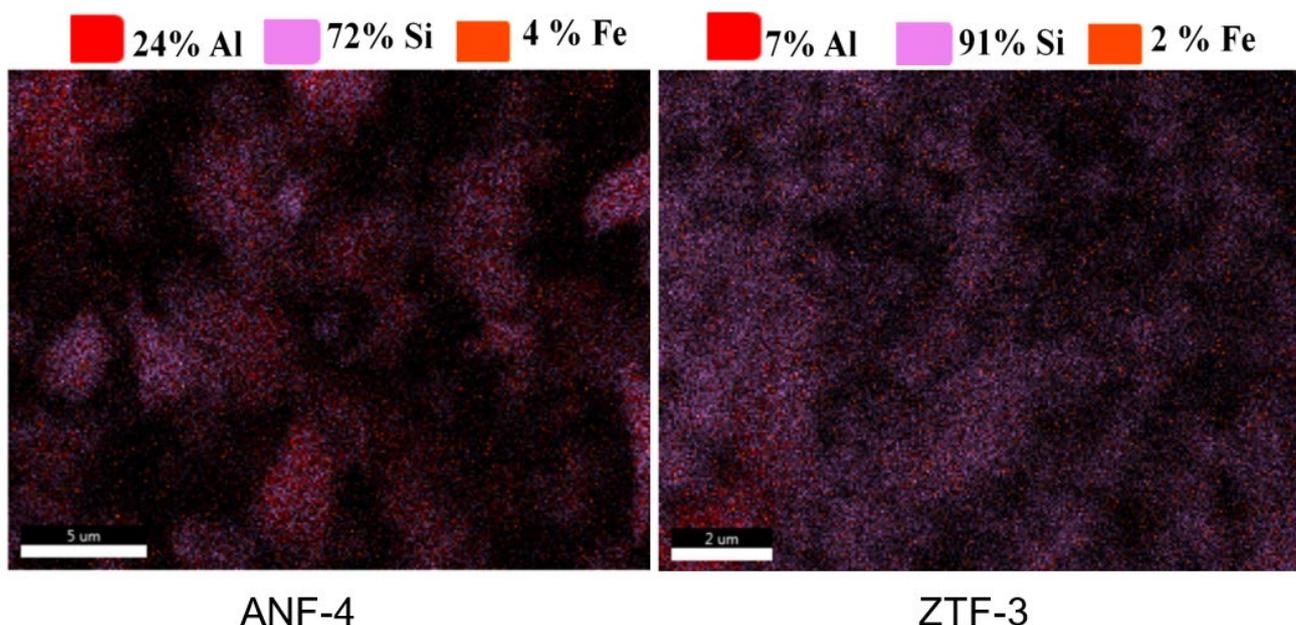


Figure 8. EDS mapping of aluminosilicates and ZSM-5 impregnated by Fe³⁺.

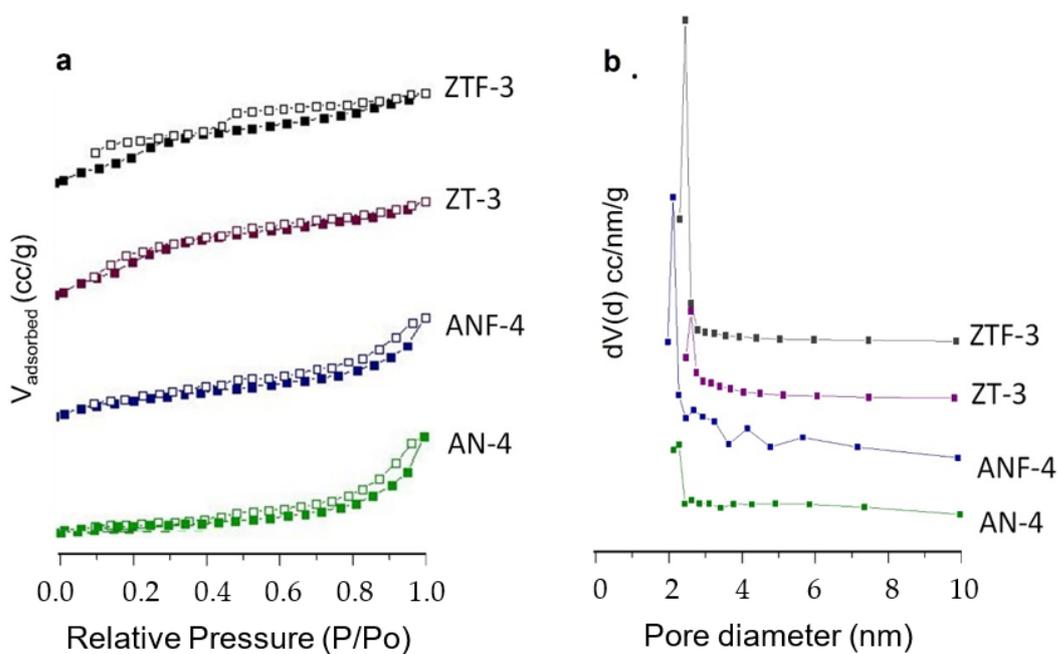


Figure 9. N₂ adsorption–desorption isotherm (a) and pore size distribution (b) of catalysts.

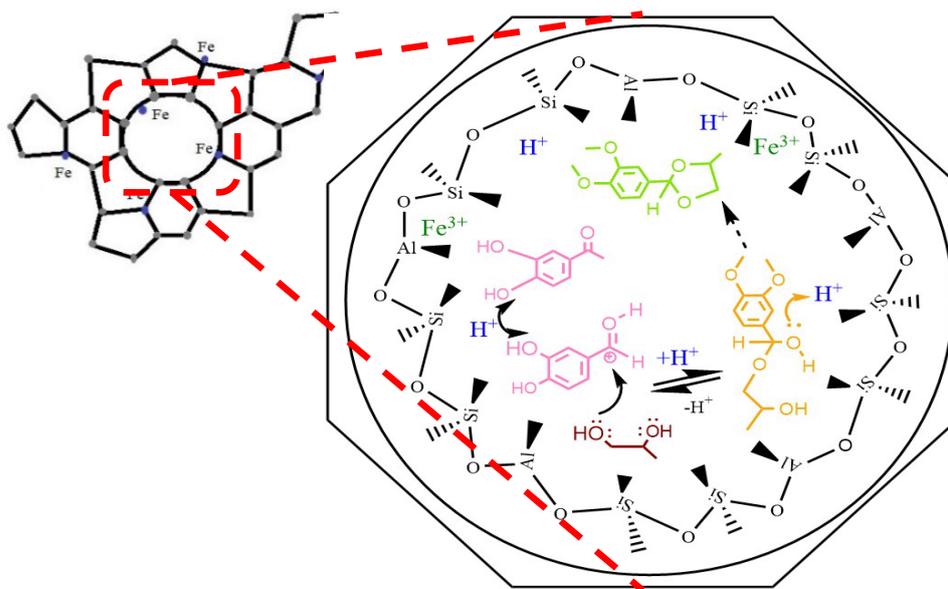
Table 2. Textural properties of aluminosilicate and ZSM-5 catalyst.

Sample	Micropore Surface Area (m ² /g)	Mesopore Surface Area (m ² /g)	Average Pore Diameter (nm)	Pore Volume (cm ³ /g)
ANF-4	154.5	81.8	3.5890	0.1405
AN-4	21.6	43.5	3.5680	0.0889
ZTF-3	37.1	66.9	3.5820	0.0589
ZT-3	26.9	32.2	3.5790	0.0395

2.2. Catalytic Activity Test

The catalytic performance of the catalyst was evaluated through acetalization of 3,4-dimethoxybenzaldehyde with propylene glycol. The acetalization reaction was con-

ducted at 105 °C for 4 h using toluene as solvent and nitrobenzene as internal standard. The sample analysed by GC-MS. The reaction mechanism is shown in Scheme 1. The formation of carbocation on the carbonyl group of 3,4-dimethoxybenzaldehyde (pink) is catalysed and takes place on the acid sites of the catalyst. Then, the nucleophilic oxygen of propylene glycol interacts with the previously formed carbocation species. After deprotonation, hemiacetal (orange) was formed, which further reacted with the hydroxyl group on propylene glycol. Afterwards, cyclodehydration eliminate water molecule and produced 2-(3,4-dimethoxy-phenyl)-4-methyl-1,3-dioxolane (green) [24].



Scheme 1. Mechanism of formation of 2-(3,4-dimethoxy-phenyl)-4-methyl-1,3-dioxolane.

The catalytic result of catalysts (Figure 10) showed that the conversion of 3,4-dimethoxybenzaldehyde by aluminosilicate (AN-4) was 32.2% higher than ZSM-5 (ZT-3). ZT-3 showed negligible activity with no conversion observed on ZT-3 is 0%. The different activity was due to the presence of higher mesoporosity in the hierarchical catalyst especially for reactions with bulky reactant molecules. The relatively small micropores of this catalyst significantly limit mass transfer to/from the active sites, decrease accessibility and inner diffusion path [25]. Moreover, Fe^{3+} addition significantly enhances the catalytic performances both ANF-4 and ZTF-3. This result was in accordance with the higher surface and total pore volume of the catalyst (Table 2). Other researcher also reported that Fe^{3+} is acidic and the use of acidic co-catalysts has proven to be a feasible option because it narrows the distribution of products into the gasoline/diesel range by combining hydrocracking, olefin oligomerization, alkylation, branching, and aromatization reactions [26]. All the catalysts also indicated high performance for acetalization reaction with the selectivity towards the products (2-(3,4-dimethoxy-phenyl)-4-methyl-1,3-dioxolane) reaching 100%.

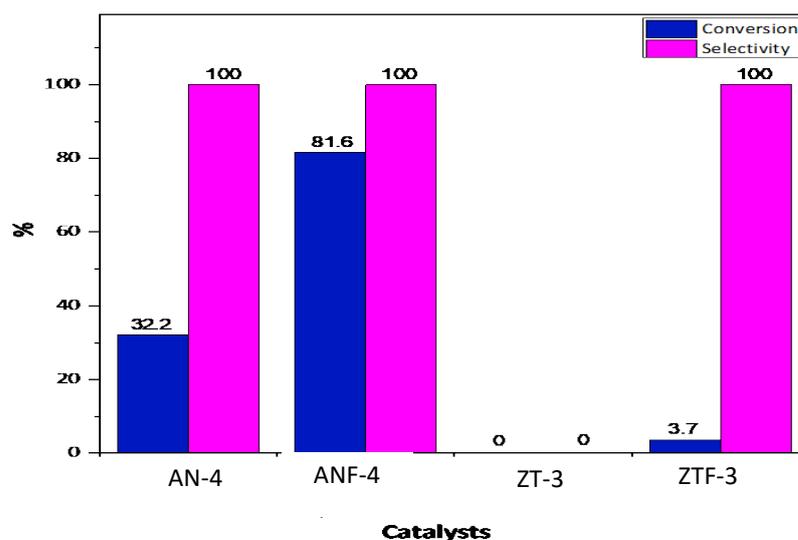


Figure 10. Conversion of 3,4-dimethoxy benzaldehyde by catalysts to form acetal and selectivity to 2-(3,4-dimethoxy-phenyl)-4-methyl-1,3-dioxolane.

3. Materials and Methods

3.1. Materials

Kaolin used in this study was obtained from Blitar, East Java (Indonesia). Colloidal silica (LUDOX[®] 40 wt. % SiO₂ in water, Aldrich, St. Louis, MO, USA) was used to increase the Si/Al mole ratio. Sodium hydroxide (NaOH; Merck, ≥97%), tetrapropylammonium hydroxide (TPAOH; Merck, Darmstadt, Germany, 40%), were used as the base in the alkali treatment process. Hydrochloric acid (HCl; Merck, 37%) and iron powder were used to make iron (III) chloride solution. Distilled water was also used in the catalysts preparation. Ammonium hydroxide (NH₄OH; Merck, 32%), ammonium acetate (CH₃CO₂NH₄; Merck, 99%), were used in catalyst activation. 3,4-dimethoxybenzaldehyde, propylene glycol, toluene (C₆H₅CH₃; Merck, 99.9%), nitrobenzene (C₆H₅NO₂; Merck, 99%), and paraffin were used in catalytic reaction. All the materials were used directly without purification.

3.2. Synthesis of Catalysts

Before synthesizing catalysts, kaolin was washed with distilled water with 1:8 ratio by centrifugation, repeatedly. This process produced three layers, i.e., water, kaolin, and impurities, thus allowing the separation of kaolin from impurities. Kaolin, in the second layer, was collected and dried in an oven at 105 °C for 24 h. Afterward, kaolin was characterized using X-ray diffractometer (XRD) and X-ray fluorescence spectrometer (XRF) to obtain the composition prior to synthesizing catalysts.

Aluminosilicates were synthesized following the modified method previously reported by Qoniah, et al. [15]; Gonçalves, et al. [16]; dan Sreenivasulu, et al. [27]. The molar composition of aluminosilicate was set at 1 SiO₂: 0.00625 Al₂O₃: 0.2 OH (base): 38 H₂O. 0.4902 g kaolin was mixed with 28.5 mL colloidal silica and stirred for 30 min with a magnetic stirrer. Colloidal silica was added to adjust the ratio of Si/Al: 80. NaOH solution was prepared by dissolving 2.02 g NaOH with 154 mL water. TPAOH solution was prepared by diluting 25 mL TPAOH in 139 mL water. The alkali treatment was carried out by mixing the washed kaolin with the base solution (NaOH or TPAOH), then stirred for 15 h in room temperature to age.

After the alkali treatment process, the mixture was hydrothermally heated in a closed system under various conditions as summarized in Table 3. The mixture was washed and separated by centrifugation, then dried in the oven at 80 °C for 24 h. After that, the collected sample was calcined at 550 °C for 1 h in N₂ and then 5 h in the air.

Table 3. Sample annotation and the variation of synthesis's parameter.

Sample Code	Base		Fe ³⁺ Addition	Hydrothermal	
	NaOH	TPAOH		Time (h)	Temp (°C)
AN-1	✓			12	60
				24	80
AT-1			✓	12	60
				24	80
AN-2	✓			24	60
				48	80
AT-2			✓	24	60
				48	80
AN-3	✓			24	80
AT-3			✓	24	80
AN-4	✓			36	80
AT-4			✓	36	80
ANF-4	✓			36	80

✓ = added.

ZSM-5 was synthesized following the method previously reported by Hartati, et al. [28] and Soltani, et al. [29]. The molar composition of aluminosilicate was set at 0.25 SiO₂: 0.00156Al₂O₃: 0.05 OH (base): 9.5 H₂O. The main steps in the ZSM-5 synthesis were the same as those in aluminosilicate synthesis but at the different hydrothermal conditions. The synthesis routes of ZSM-5 are summarized in Table 4.

Table 4. Sample annotation and variation of synthesis's parameter.

Sample Code	Base		Fe ³⁺ Addition	Hydrothermal	
	NaOH	TPAOH		Time (h)	Temp (°C)
ZN-1	✓			48	80
ZN-2	✓			72	80
ZN-3	✓			96	80
ZT-1		✓		48	80
ZT-2		✓		72	80
ZT-3		✓		96	80
ZTF-3		✓	✓	96	80

✓ = added.

The resulting aluminosilicate and ZSMS-5 were proceeded with stirring for Fe³⁺ addition by mixing 1 g catalyst with 10 mL of 1 M FeCl₃ solution (made by dissolving iron powder with concentrated HCl). The mixture was stirred for 3 h at 80 °C and aged at room temperature for 12 h. Afterward, the mixture separated, and the collected solids was dried in oven. This process was repeated two times. After that, the solids were calcined at 550 °C fo 6 h.

3.3. Catalyst Characterization

XRF (Philips Analytical Minipal 4) was used to determine the composition of kaolin prior to the ZSM-5 synthesis. The structure and crystallinity of the catalysts were analysed using Philips X'pert X-ray Diffractometer XRD instrument with Cu K α radiation with a step size of 0.02° and a counting time of 10 s. The diffractogram were collected in the 2 θ range of 5–50°. The Fourier transform infrared (FTIR) spectra were recorded by FTIR spectrometer (Shimadzu IR Tracer-100. The pore distribution, pore volume, and surface area of catalysts were measured using nitrogen physisorption analyser (Quantachrome TouchWin v1.2). The particle size was analysed using a dynamic light scattering (DLS) instrument. SEM images and elemental analysis of the samples were carried out with SEM-EDS (Carl Zeiss Evo MA 10).

3.4. Catalytic Activity Test in Acetalization

The cation exchange process activated the catalysts before the catalytic testing. The cation exchange was carried out using 0.5 g catalyst and 20 mL ammonium acetate 0.5 M. The mixture was added in the reflux and heated at 60 °C for 3 h. The mixture was separated using centrifugation and the resulting solid was dried in oven at 110 °C for 12 h, followed by calcination at 550 °C for 6 h. Afterward, the catalyst was heated in the oven at 100 °C for 24 h for activation. The acetalization reaction was carried out by mixing 0.1861 g of 3,4-dimethoxybenzaldehyde, 0.1634 g propylene glycol, 0.02 g catalyst, 20 mL toluene as solvent, and 100 µL nitrobenzene as internal standard. The mixture was refluxed in a three-neck round bottom flask at 105 °C for 4 h. The sample analysed by GC-MS. The conversion of substrate (3,4-dimethoxybenzaldehyde) was determined based on Equation (1) [24].

$$\text{Conversion (\%)} = \frac{\text{DMB}_i - \text{DMB}_f}{\text{DMB}_i} \times 100 \quad (1)$$

where DMB_i —initial concentration of 3,4-dimethoxybenzaldehyde; DMB_f —final concentration of 3,4-dimethoxybenzaldehyde.

The selectivity of product (2-(3,4-dimethoxy-phenyl)-4-methyl-1,3-dioxolane) was calculated based on Equation (2) [24].

$$\text{Selectivity (\%)} = \frac{\text{peak area of product}}{\text{peak are for all the products}} \times 100 \quad (2)$$

4. Conclusions

In this study, the potential of low-grade kaolin contaminated with quartz was investigated for the synthesis of aluminosilicate and ZSM-5. Aluminosilicate with high purity was not produced from kaolin; meanwhile, pure ZSM-5 was produced from synthesis using TPAOH at 80 °C for 96 h. However, aluminosilicate showed higher activity as acetalization catalyst than ZSM-5. Addition of Fe^{3+} to the aluminosilicates and ZSM-5 improved the performance of the catalysts in the acetalization reaction.

Author Contributions: Conceptualization, H.H. (Hartati Hartati), H.H. (Hartono Hartono), H.B. and D.P.; methodology, Q.A., N.H.S. and D.Z.M.; formal analysis, N.H.S. and D.Z.M.; investigation, N.H.S. and D.Z.M.; data equation, H.H. (Hartati Hartati), Q.A., P.B.D.F. and H.B.; writing—original draft preparation, H.H. (Hartati Hartati), P.B.D.F. and R.E.N.; writing—review and editing, H.H. (Hartati Hartati), Q.A., H.B., D.P. and N.A.S. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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