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Bulletin of Chemical Reaction Engineering & Catalysis, 20 (1) 2025, 156-165

Research Article

Molar Ratio Comparison of Ti-Zr as Catalyst Support of Bentonite in Esterification Reaction

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Received: 23th November 2024; Revised: 11th February 2025; Accepted: 15th February 2025
Available online: 20th February 2025; Published regularly: April 2025

Abstract

Natural bentonite from Pacitan - Indonesia as a support in the preparation of Ti and Zr-pillared metal catalysts (Ti-Zr/bent) for esterification reaction were studied. The preparation of Ti-Zr/bent catalyst was prepared to find out the effect of molar ratios (Ti:Zr) where an investigation was performed in the esterification of waste cooking oil. The catalyst was varied as follows: 0.5:1 (Ti-Zr-1/bent), 1:1 (Ti-Zr-2/bent), 1.5:1 (Ti-Zr-3/bent), 2:1 (Ti-Zr-4/bent), and 5:1 (Ti-Zr-5/bent) were used to determine the yield. The reaction was carried out for 3 hours at 150 °C and a pressure of 40 bar N_2 gasses. The result of the Ti-Zr/bent catalyst was given increasing significantly for surface area of 133–147 m^2/g compares to bentonite 27 m^2/g and 10 times of acidity. The best catalyst was shown in 2:1 of ratio Ti:Zr (molar) on esterification reaction with succesfuly performed about 80.40% of yield.

Keywords: Bentonite; Esterification; Pillared clay; Titanium; Waste cooking oil

How to Cite: Firmansyah, S., Agustian, E., Rinaldi, N., Widiarti, N., Hanifah, Y., Maisaroh, M., Sulaswatty, A. (2025). Molar Ratio Comparison of Ti-Zr as Catalyst Support of Bentonite in Esterification Reaction. *Bulletin of Chemical Reaction Engineering & Catalysis*, 20 (1), 156-165. (doi: 10.9767/bcrec.20258)

Permalink/DOI: https://doi.org/10.9767/bcrec.20258

1. Introduction

The use of bentonite as a catalyst in esterification reactions has been successfully demonstrated. The addition of pillaring metals through intercalation methods was employed in this study to enhance the catalyst's performance in the esterification of waste cooking oil. Pillaring is a technique where ions, molecules, or compounds with high stability are inserted between the layers of bentonite to obtain a high pore volume [1-2]. Research on bentonite pillaring has been widely reported, including the use of a single metal or multiple metals (polycation). Single metal pillaring was performed by Taher *et al.* [2] where the use of Ti^{4+} increased the basal spacing of bentonite. Single and dual metal pillaring was also carried out by Castro *et al.* [3] where the pillaring was done using Al metal and a combination of Al-Zr, with the addition of Zr enhancing the acidity of the catalyst.

It has been reported that the pillaring metals used were Ti and Zr, which have been confirmed in previous research to be suitable for bentonite pillaring for bioidesel process. Among these studies are those by Khairina *et al.* [4] on bentonite pillaring Ti/Zr (molar ratio of 1:9) using conventional stirring for esterification reactions at 150 °C for 3 hours and 20 bar N_2 using the oleic

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acid obtained conversion of 74.83%. Research on the esterification of waste cooking oil to biodiesel using pillared bentonite as a catalyst by Agustian *et al.* [5] explained that the synthesis of the catalyst Ti/Zr (molar ratio of 1:1) with variations in sonication time has successfully pillared bentonite with an achieved conversion of 78.43% wt, while Nugraha *et al.* [6] examined bentonite pillaring using Ti-Zr (ratio molar of 1:1) with variations in reaction time and pressure for esterification. However, the research of bentonite pillaring with mixture ratio Ti/Zr has been investigated attentively with the intention of enhancing the structure and features of bentonite, but there has been limited investigation to examine the molar ratio Ti/Zr.

The selection of these two metals is based on titanium's superior mechanical properties compared to other base metals, as well as its high melting point, providing thermal stability [7-9]. Advantage of zirconium is known for its high strength and toughness, corrosion resistance, ability to provide high surface area, and ability to increase the surface acidity of bentonite, making it an ideal choice for this research. [10-11]. Bahranowski *et al.* [12] explained that the incorporation of zirconium stabilizes the anatase modification of titania by increasing the specific surface area and surface acidity due to charge imbalance from the formation of Ti-O-Zr bonds. Due to their stable activity and enhanced properties for moderate reaction conditions, solid catalysts containing double metals of Ti and Zr have limited knowledge for use as a support in bentonite. This purpose is to obtain the effect of the impregnation of bentonite with a variety of Ti ratios on the physicochemical properties of the catalyst and evaluate their activity in biodiesel production using waste cooking oil.

2. Materials and Methods

2.1 Materials

The materials used in this study include waste cooking oil sourced from street food small restaurants in a market in Central Java, natural bentonite from Pacitan, titanium(IV) propoxide ($Ti(OC_3H_7)_4$) from Aldrich, zirconium(IV) oxide chloride octahydrate ($Cl_2OZr\cdot 8H_2O$), potassium hydroxide (KOH), and sodium sulfate (Na_2SO_4) from EMSURE®. Additionally, methanol (CH_3OH) from Supelco®, hydrochloric acid (HCl) from SMART-LAB, silver nitrate ($AgNO_3$) from Applichem, phenolphthalein indicator (PP), universal indicator from MQuant®, and distilled water (H_2O) from Milli-Q were used.

2.2 Synthesis of Pillaring Bentonite with Polycations of Ti-Zr

The synthesis of titanium-zirconium modified bentonite (denoted as Ti-Zr/bent) was based on the research by Bahranowski *et al.* [12] and Agustian *et al.* [5] with several modifications. The Ti-Zr polycation was prepared by dissolving $Ti(OC_3H_7)_4$ using 5 M HCl and stirring until homogeneous, while $Cl_2OZr\cdot 8H_2O$ was dissolved using 0.4 M CH_3OH. The titanium solution and zirconium solution were mixed and stirred for 3 hours at room temperature. The molar ratios of Ti and Zr used in the study are summarized in Table 1.

A total of 3 grams of bentonite was added to 300 mL of distilled water at 60 °C and stirred for 2 hours at a temperature of 60-70 °C. The Ti-Zr polycation solution was gradually added to the bentonite suspension under continuous stirring, and stirring was continued for an additional 30 minutes without heating. The pillared bentonite suspension was sonicated for 30 minutes at 50% amplitude, followed by stirring at room temperature for 24 hours. After turning off the stirring, the suspension's pH was measured. The suspension was washed with 5 liters of distilled water at 60 °C. The pillared bentonite suspension was centrifuged at 5000 rpm for 5 minutes at 25 °C after washing. The washing process was repeated until the solution showed a negative reaction (no white precipitate formation) with 0.1 M $AgNO_3$ reagent. The pillared bentonite precipitate was dried in an oven at 110 °C for approximately 12 hours. The catalyst was ground and then calcined for 4 hours at 400 °C.

2.3 Catalyst Characterizations

The elemental analysis of bentonite and modified bentonite was conducted using X-ray fluorescence (XRF) S2 PUMA-Bruker. Surface area, pore volume, and pore size were analyzed

Table 1. Design preparation pillared bentonite with various ratios of Ti and Zr

Molar Ratio Ti: Zr	$Ti(OC_3H_7)_4$ (g)	HCl (ml)	$Cl_2OZr.8H_2O$ (g)	CH_3OH (ml)
Ti-Zr-1/bent (0.5:1)	5.68	4.0	6.45	50.0
Ti-Zr-2/bent (1:1)	8.53	6.0	4.83	37.5
Ti-Zr-3/bent (1.5:1)	10.23	7.2	3.87	30.0
Ti-Zr-4/bent (2:1)	11.37	8.0	3.22	25.0
Ti-Zr-5/bent (5:1)	14.21	10.0	1.61	12.5

using the TriStar II 3020 Version 2.00 through the BET and BJH methods. The acidity of the catalyst was also analyzed using Ammonia Temperature Programmed Desorption (TPD-NH_3) with the New Autochem II, utilizing a mixed gas concentration of 5% NH_3 (He balance, v/v). X-ray diffraction (XRD) Rigaku was employed in the range of 2θ = 5 - 80˚ with Cu-Kα radiation (λ = 1.541862) to determine the crystallinity of the catalyst and provide information regarding the success of the pillaring process.

2.4 Esterification Reaction

As the Figure 1, fatty acid methyl ester was occurred in the reaction esterification of fatty acid with present methanol. The Ti/Zr Bent as a catalyst, weighing 0.25 g (5% of the reactant weight), was oven-dried at 100˚C for 30 minutes. Methanol and waste cooking oil were weighed, amounting to 11.33 g and 5 g, respectively. The catalyst was removed from the oven and allowed to cool at room temperature, then methanol was added to the catalyst.

The experiment esterification reaction in batch close reactor was presented in Figure 2. The waste cooking oil and a magnetic stirrer directly placed into the batch close reactor (c) and followed by the pillared bentonite-methanol mixture. The reactor was sealed and locked. Nitrogen gas (a) was flushed into the reactor, vented, and refilled to reduce other gases present in the reactor. The nitrogen gasses was maintained (b) at 40 bar and cek it to ensure no gas leakage. The sample was stirred (d) and set the fixed temperature (e) at 150˚C for a 3-hour reaction [6]. After completion, the mixture was transferred into a tube centrifuge for phase separation. The methyl ester formed in middle layer, catalyst in lower layer and methanol – water – glycerol mixture that was not reacted in upper layers. Then the methyl ester layer was evaporated to release unreated methanol-water. The product methyl ester was analyzed using a Gas Chromatography-Mass Analyzer (GCMS) Agilent 1909 IS with an HP-5MS column. The condition of initial temperature is 40 °C, hold time of 1 min and post run is 300 °C with sample injection is 1 µL. The methyl ester yield was calculated using equation (1) [13] :

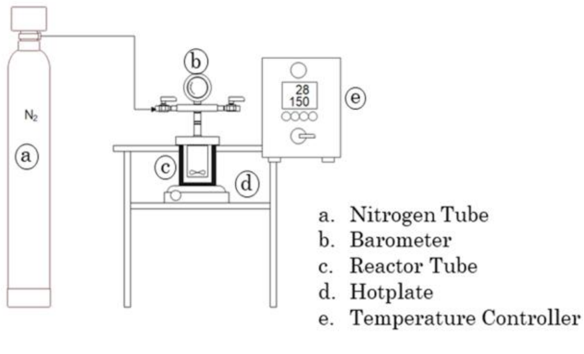

Figure 2. Schematic of batch close reactor with 100 mL capacity for this study

$$Yield\ (\%) = \frac{\%\ FAME\ area\ from\ GCMS\ x\ weight\ of\ product}{weight\ waste\ cooking\ oil}\ x\ 100\% \qquad (1)$$

3. Results and Discussion

3.1. X-Ray Fluorescence

The analysis using X-ray fluorescence (XRF) provided data on the elemental composition of the samples, specifically for bentonite and the Ti-Zr/bent catalyst. Bentonite is a clay mineral primarily composed of montmorillonite, which consists of two silica layers in a tetrahedral structure with an octahedral alumina layer sandwiched between the silicas [14]. Bentonite is formed from volcanic activity and is characterized by its large surface area, good swelling properties, and high ion exchange capacity within its interlayer spaces [15-16]. The surface of bentonite exhibits both Brønsted and Lewis acidity, making it suitable for use as a catalyst [16]. The relatively low cost and environmental friendliness of bentonite also make it an advantageous material [17].

Table 2 shows that the elemental composition by XRF data was obtained with some pillared bentonite led to a reduction in the content of SiO_2 and Al_2O_3, which are the primary components of bentonite. On the other hand, the increase in TiO_2 and ZrO_2 corresponds to the addition of polycations, with a higher Ti content leading to a lower Zr addition. The decrease in CaO and Na_2O is due to cation exchange with the intercalated metals, Ti and Zr, which occurs because of differences in bond affinity [18]. Natural bentonite contains many other compounds, which are discussed in this article.

Abdullahi *et al.* [19] reported the composition of bentonite from Ashaka and Tango, which consists of SiO_2, Al_2O_3, Fe_2O_3, CaO, Na_2O, MgO, K_2O, TiO_2, and P_2O_5. Kumar *et al.* [20] compared

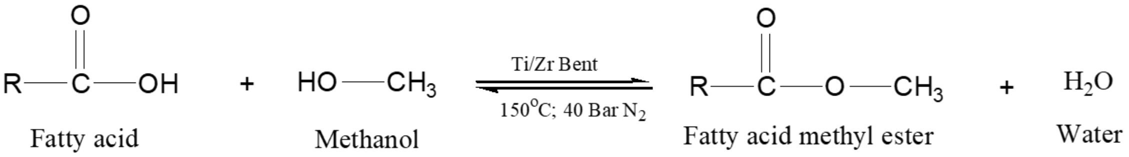

Figure 1. Reaction esterification fatty acid with methanol using Ti/Zr Bent catalyst

the composition of kaolin with sodium bentonite, revealing the chemical content of SiO_2, Al_2O_3, K_2O, Fe_2O_3, TiO_2, MgO, Na_2O, CaO, P_2O_5, Cr_2O_3, Mn_2O_3, and NiO. Bentonite analysis by Ibrahim *et al.* [21] provided a composition that includes SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, Cl, and SO_3. The specific composition of natural bentonite varies from location to location, but common elements include SiO_2, Al_2O_3, Fe_2O_3, CaO, Na_2O, MgO, K_2O, TiO_2, and P_2O_5.

3.2. Surface Analysis

Surface analysis using the BET and BJH methods was conducted in this study. The Surface Area Analyzer (SAA) is the instrument utilized for determining the surface area and pore distribution of a material [22]. The Brunauer-Emmett-Teller (BET) theory is employed to estimate specific surface area through gas adsorption. The Barrett-Joyner-Halenda (BJH) method is also used to obtain pore size distribution via gas adsorption-desorption [23]. Table 3 indicates that the surface area of the catalyst increased up to four times compared to raw bentonite. The highest surface area was obtained for the Ti-Zr-1/bent catalyst, measuring 147.49 m²/g, while the smallest was for the Ti-Zr-3/bent catalyst, measuring 131.80 m²/g. The pillared bentonite became a porous material due to the formation of a significant number of microporous structures between the layers of bentonite sheets, as evidenced by the increased surface area after pillaring, even though the pore diameter decreased post-pillarization [4,24]. Table 3 shown that the presents data on pore volume and pore size bentonite and pillared bentonite. It is noted that all catalysts are capable of increasing pore volume while reducing pore size. The trend of increasing Ti molar ratios enhances pore size but decreases pore volume. Based on the indicated pore sizes, both bentonite and the catalysts fall within the mesoporous category, as they are within the range of 2 – 50 nm [25].

It is known that isotherms are classified into six types; however, in recent decades, this classification has expanded to eight types. Figure 2 shows the adsorption-desorption isotherm curves, where bentonite falls under type V, while the catalyst is categorized as type IV(a). Type V exhibits weak adsorbent-adsorbate interactions, whereas type IV(a) involves capillary condensation accompanied by hysteresis, occurring when pore width exceeds a certain critical width. For nitrogen and argon adsorption in cylindrical pores at 77 K and 87 K, respectively, hysteresis begins to appear for wider pores [27].

Table 2. Elemental composition of Bentonite and pillared bentonite with various concentrations

Catalyst	Elemental Composition (%wt)						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	TiO_2	ZrO_2
Bentonite	50.10	27.40	13.50	1.70	1.50	1.30	0.00
Ti-Zr-1/bent (0.5:1)	40.90	22.10	12.10	0.60	0.10	5.80	15.60
Ti-Zr-2/bent (1:1)	39.50	21.40	13.30	0.70	0.00	9.30	13.20
Ti-Zr-3/bent (1.5:1)	41.00	22.30	12.90	0.50	0.20	10.00	10.30
Ti-Zr-4/bent (2:1)	39.10	22.10	12.80	0.40	0.20	12.80	10.00
Ti-Zr-5/bent (5:1)	38.00	21.20	14.70	0.50	0.00	16.50	6.40

Table 3. Surface area, pore volume, pore size, and acidity of bentonite and pillared bentonite.

Catalysts	Surface Area		Pore Volumes	Pore Size	References
	BET Surface Area (m²/g)	t-Plot micropore area (m²/g)	t-Plot micropore volume (cm³/g)	Adsorption average pore width (4V/A by BET) (nm)	
Bentonite	27.12	-	0.002	11.86	This study
Ti-Zr-1/bent (0.5:1)	147.49	44.14	0.023	3.81	This study
Ti-Zr-2/bent (1:1)	138.93	30.63	0.016	4.09	This study
Ti-Zr-3/bent (1.5:1)	131.80	26.09	0.013	4.31	This study
Ti-Zr-4/bent (2:1)	138.93	18.15	0.009	4.13	This study
Ti-Zr-5/bent (5:1)	133.54	4.45	0.002	4.62	This study
TiO_2	76.6	-	0.44	-	[26]
ZrO_2	2.70	-	-	16.62	[13]
Ti/bentonite	196.89	2.66	0.24	4.73	[5]
Zr/Bentonite	57.04	107.97	0.06	4.79	[5]

Temperature-programmed desorption of Ammonia (NH_3-TPD) is an instrument used to determine the distribution of acid sites present in the sample [28]. The TPD method operates by drying the sample under a helium flow, cooling it, and saturating it with ammonia (10% NH_3 in He). The sample is then returned to the helium flow, where the use of helium is evaluated to effectively remove ammonia from the pores, leaving only the molecules adsorbed onto the sample [29]. Table 4 presents the acidity dataand surface acid site distribution for both bentonite and the catalysts, revealing that the acidity of all catalysts is greater by up to eight times that of bentonite. The trend in catalytic acidity increases up to Ti-Zr-3/bent, followed by a decrease in Ti-Zr-4 and Ti-Zr-5 catalysts. This is associated with the reduced amount of Zr added during synthesis and the decrease in pore volume. Among the catalysts presented, Ti-Zr-4/bent is the most efficient due to its high acidity.

The amount of the distribution acidity was calculated based on the relatives areas of corresponding band of NH_3-TPD analysis as follows in Equation (2):

$$Q = Q_N \; x \; \frac{A}{A_T} \; x \; 100\% \tag{2}$$

where, Q (mmol/g) is the quantity of desorbed NH_3 corresponding to the TPD peak of relative area A, Q_N (mmol/g) is the total amount of desorbed NH_3, A is the corresponding deconvolution area of one NH_3-desorption peak, and A_T is the total deconvolution area of all the NH_3-desorption peaks. Three different types of desorption peaks from 100 °C to 800 °C were observed, which correspond to weak (100° C–250 °C), medium (250 °C–500 °C), and strong acid (500 °C–800 °C) [30].

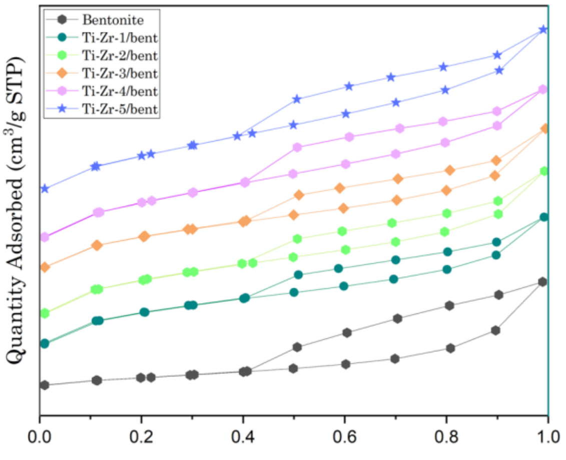

Figure 2. N_2 adsorption isotherm curves for bentonite and various pillared bentonite

Table 4 was defined acid site as weak, medium and strong at desorption temperature 100 to 800 °C. The medium-strength acid sites were distributed for bentonite and all Ti-Zr/bent catalyst dominate in weak to medium strength acid sites. Strong-strength acid sites emerged and the quantity of medium-strength acid sites increased after heating, but the quantity of weak-strength acid sites reduced. Strong and medium-strength acid sites were most abundant in Ti-Zr-1/bent (0.5:1) (1.55 mmol/g) and Ti-Zr-4/bent (2:1) (1.83 mmol/g). Furthermore, our investigation demonstrates that pillaring Ti and Zr into bentonite could significantly raise the surface acidity of modified bentonite samples, which is consistent with the findings of the literature [5]. Similar to other references, Ti-Zr/Bent exhibits the phenomena of enhanced surface acidity. The OH groups connected to the Al ion pillars (Al–OH) constitute the weak and medium acid sites, whereas the OH groups attached to the tetrahedrally coordinated Al ions are linked to the strong acid sites [31].

3.3. X-Ray Diffraction

X-ray diffraction (XRD) analysis is employed to identify the structural changes occurring in bentonite after being pillared with titanium (Ti) and zirconium (Zr). Small or amorphous crystals generate very broad signals in XRD, making accurate quantification challenging [32]. The presence of highly intense peaks in the XRD of the

Table 4. Surface acid site distribution and total acidity obtained from bentonite and Ti-Zr/Bent of catalyst

Sample Name	Acidity (mmol/g)			
	Weak (100-250 °C)	Medium (250-500 °C)	Strong (500-800 °C)	Total
Bentonite	0.00	0.22	0.22	0.43
Ti-Zr-1/bent (0.5:1)	0.61	0.88	1.55	3.04
Ti-Zr-2/bent (1:1)	1.41	1.61	0.49	3.51
Ti-Zr-3/bent (1.5:1)	1.54	1.61	0.46	3.62
Ti-Zr-4/bent (2:1)	1.67	1.83	0.73	4.22
Ti-Zr-5/bent (5:1)	0.93	1.42	0.87	3.22

tested samples confirms crystalline behavior [33]. The bentonite sourced from Pacitan, Indonesia, is detected as montmorillonite with 13 specific peaks at $2\theta = 6.08^\circ$; 12.29°; 19.907°; 21.03°; 24.85°; 26.603°; 28.72°; 35.41°; 36.56°; 38.4°; 43.363°; 54.87°; and 62.08° [Ref. Code 96-900-2780]. The incorporation of Ti and Zr into the bentonite structure resulted in the formation of metal oxide pillars between the montmorillonite layers, enhancing structural and thermal stability. Khairina *et al.* [4] noted that the bentonite peaks are located at low angles in the XRD analysis; however, in this study, data collection at low angles was not feasible due to instrument limitations. The absence of the peak at $2\theta = 6.08^\circ$ (d_{001} = 14.53 Å) is obtained and the result was indicated successful pillaring. It has been reported that an increase in interlayer distance suggests the success of the pillaring process [12]. This is further supported by the disappearance of several peaks and the emergence of new peaks at 34.87°, 50.09°, and 59.89°. An analysis comparing the catalyst database and the metals used for pillaring, such as Titanium anatase, Titanium rutile, and Zirconium oxide, was also conducted. The presence of zirconium oxide is confirmed in the catalyst through peaks at $2\theta = 34.87^\circ$ and 50.09° [Ref. Code 96-210-0389]. Titanium anatase [Ref. Code 96-900-9087] and Titanium rutile [Ref. Code 96-900-7532] were also utilized; the presence of Ti rutile was not detected, with only Ti anatase being observed at $2\theta = 38.35^\circ$, 54.03°, and 62.17°. Other species detected in the Ti-Zr-2/bent catalyst sample include quartz and ZrTiO. Quartz, a silica oxide with a hexagonal crystal system, was confirmed at $2\theta = 20.80^\circ$, 26.62°, 50.09°, and 59.89° [Ref. Code 96-900-9667]. The species ZrTiO was also abundantly present in the catalyst, appearing at $2\theta = 12.3^\circ$, 24.86°, 34.87°, 38.35°, 50.09°, 59.89°, and 62.17° [Ref. Code 96-100-8698].

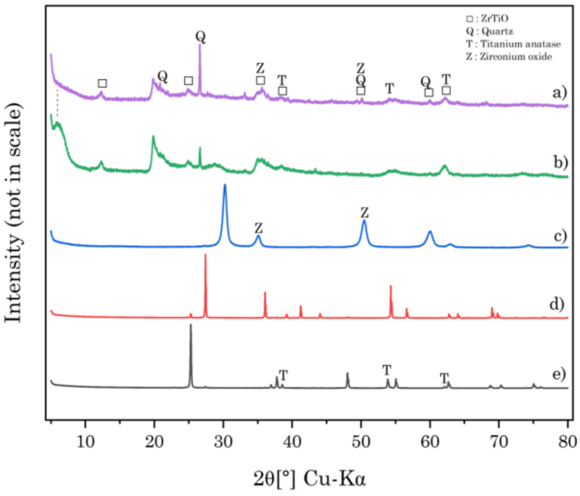

Figure 3. XRD pattern of a) Ti-Zr-2/bent, b) Bentonite, c) Zirconium oxide, d) Titanium rutile, and e) Titanium anatase

Anatase TiO_2 differs from the rutile phase in that it has a larger surface area and a higher density of surface hydroxyl groups. The protonation of carbonyl groups in esterification reactions depends on these surface hydroxyl groups reacting as Brønsted acid sites. More active sites for reactant adsorption are made available by the larger surface area, which speeds up the esterification process. Anatase TiO_2 can be added to Ti-Zr/bentonite catalysts to provide synergistic effects that improve catalytic performance even further. When Ti and Zr are combined, a stronger catalytic framework can be produced, increasing heat stability and offering more active sites. In order to prevent agglomeration and maintain a high surface area, the bentonite support can also help TiO_2 and ZrO_2 particles spread [34-35]. Overall, the addition of pillaring metals does not damage the bentonite structure but rather opens gaps between its layers, as observed in the graph, which shows minimal changes.

3.4. Catalytic Activity

Esterification is a process that converts lipids by reacting free fatty acids (FFA) with alcohol to produce fatty acid methyl esters (FAME) and water [36]. Waste cooking oil has high acidity due to prolonged heating at high temperatures, extended use, storage, and processing [37-38]. In the transesterification reaction of waste cooking oil, free fatty acids react with the catalyst to form soap, which reduces the efficiency of the process and results in low biodiesel yields; therefore, the esterification reaction is chosen for this study [38]. The esterification reaction is classified as a reversible reaction, as one mole of oil requires one mole of methanol. Thus, excess methanol is provided to drive the reaction toward the right and produce more biodiesel [39]. The GC-MS instrument is utilized to confirm the catalytic activity of the catalyst. GC-MS analysis displays a chromatogram of the compounds present in the sample, where the x-axis represents retention time and the y-axis indicates the abundance of the compounds. The quantity of compounds contained in the sample is interpreted as the area under the curve in the GC-MS analysis.

Table 5 presents that the results of the FAME analysis using GC-MS, indicating that the amount of palmitate is the most dominant among all the formed FAMEs, averaging above 30%. The second most dominant compound is methyl oleate; however, in the cases of catalysts Ti-Zr-4/bent gave high area in 50.31%. The total FAME results are satisfactory, averaging above 90%. Two types of FAME that are often found in biodiesel made from Waste Cooking Oil (WCO) are palmitate acid methyl ester and stearate acid methyl ester. The catalyst's active site and the -OH group in FAME can interact to speed up the reaction and enhance conversion [13]. The successful conversion of WCO into biodiesel proved by the synthesis of a methyl ester.

The impact of a pillared bentonite catalyst on the yields of methyl ester from used cooking oil with existing methanol is shown in Table 6 and Figure 4. When compared to Ti-Zr-5/bent, Ti-Zr-3/bent, Ti-Zr-1/bent, and Ti-Zr-2/bent (76.91%, 75.86%, 68.29%, and 57.79%), the maximum yield, 80.40%, was accordingly achieved from the Ti-Zr-4/bent catalyst. The esterification reaction is complex; thus, in order to speed it up, the temperature must be adjusted. However, waste cooking oil and methanol lose their ability to dissolve; they do this by decreasing the viscosity and diffusivity of their combination in the liquid phase (oil/methanol). Therefore, the resistance between the two chemicals reduces and the yield is very close to the catalytic activity with Wen *et al.*, although the fact that the Ti-MgO catalyst produced 85.3% yields of FAME at 150 °C, 6 hours, and 5% catalyst loading [26].

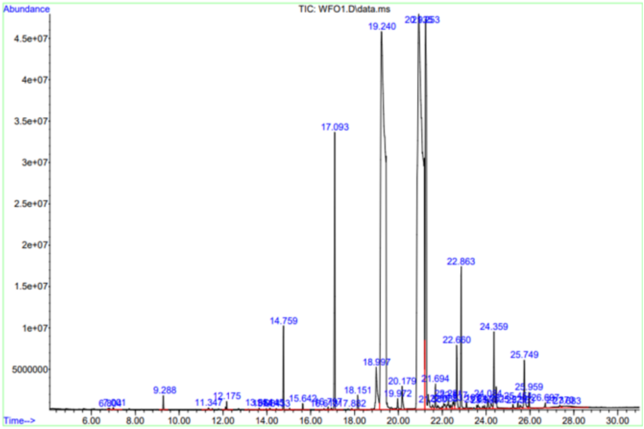

Figure 4. Chromatogram of FAME by Ti-Zr-2/bent of catalyst.

The Ti-Zr-4/Bent catalyst's larger acidic active sites (4.22 mmol/g) and bigger surface area (138.93 m²/g) enhanced easier diffusion of nitrogen gasses into the particles. On the other hand, the surface areas of Ti-Zr-1/Bent, Ti-Zr-2/Bent, Ti-Zr-3/Bent, and Ti-Zr-5/Bent were 147.49 m²/g, 138.93 m²/g, 131.80 m²/g, and 133.54 m²/g, with acidity around 3.04 mmol/g, 3.51 mmol/g, 3.62 mmol/g, and 3.22 mmol/g, respectively. A mixture of waste cooking oil and methanol can rapidly transition from a two-phase to a single phase due to the substantial drop in methanol's dielectric constant. The shape of liquid methanol can be explained by its inherent polarity and hydrogen bonding. As methanol moves into a condition of low surface tension, its polarity will decrease because hydrogen bonds become weaker at higher temperatures. Nonpolar triglycerides can be readily dissolved in nitrogen gasses due to their hydrophobic nature and lower dielectric constant.

Table 5. The composition of methyl ester (%) with various catalyst-pillared bentonite by GC-MS analysis.

Catalyst	FAME Components (%)							
	Methyl Octanoate	Methyl Dodecanoate	Methyl Myristate	Methyl Penta-decanoate	Methyl Palmitate	Methyl Hepta-decanoate	Methyl Oleate	Methyl Stearate
Ti-Zr-1/bent (0.5:1)	0.07	0.44	1.90	0.10	35.00	0.23	48.79	9.62
Ti-Zr-2/bent (1:1)	0.15	0.02	3.44	0.21	32.35	0.45	41.51	10.31
Ti-Zr-3/bent (1.5:1)	0.07	0.36	1.62	0.08	37.04	0.19	49.94	7.86
Ti-Zr-4/bent (2:1)	0.07	0.38	1.62	0.08	37.35	0.19	50.31	7.40
Ti-Zr-5/bent (5:1)	0.07	0.43	1.88	0.10	36.22	0.23	49.28	9.25

Table 6. Summary of reaction conditions biodiesel production.

Catalyst	Reaction Conditions						References
	Temperature (°C)	Pressure (bar)	Time (h)	Amount catalyst (%)	Yields (%)	FAME Conversion (%)	
Ti-Zr-1/bent (0.5:1)	150	40	3	5	68.29	-	This study
Ti-Zr-2/bent (1:1)	150	40	3	5	57.79	-	This study
Ti-Zr-3/bent (1.5:1)	150	40	3	5	75.86	-	This study
Ti-Zr-4/bent (2:1)	150	40	3	5	80.40	-	This study
Ti-Zr-5/bent (5:1)	150	40	3	5	76.91	-	This study
ZrPiLC	100	6.5 MPa CO_2	6	5	-	74.65	[5]
TiPiLC	100	6.5 MPa CO_2	6	5	-	70.91	[5]
ZrO_2-SO^{2+}	200	20 MPa	4 min		97.9	-	[40]
TiO_2	150	-	6	5	10		[26]

Bahranowski *et al.* [12], state that the interchange of cations from Zr and Ti polycations with Zr^{4+} and Ti^{4+} cations in the bentonite interlayer during the pillarization process aids in the development of many acid sites. The pillarization process in pillared bentonite increases the accessibility of protons that serve as an acid site source in the bentonite interlayers by broadening the layer structure. Because Ti-Zr/Bent catalysts have the potential to produce high methyl ester yields, they have shown promising findings when utilized as heterogeneous catalysts for esterification.

4. Conclusion

The synthesis of Ti and Zr pillaring bentonite was investigated successfully. The specific surface area of Ti to Zr increased five times, the basal spacing of pillared bentonite was increased, the surface morphology of pillared bentonite changed significantly, resulting in the formation of small-sized layers, and the total acidity increased ten times when compared to bentonite. The catalyst Ti-Zr-4/bent has 138.93 m^2/g surface area and 4.22 mmol/g acidity, leading other variants. The catalytic results showed the yield was 80.40% at 150°C, 3 hours, 40 bar, and 5% Ti-Zr-4/bent catalyst. Comparing the Ti-Zr/bent catalyst to the esterification process in general, the test showed good conversion at moderate temperature when waste cooking oil was esterified to biodiesel under N gas conditions.

Acknowledgment

The research was funded by Rumah Program Grand from the Research Organization for Nanotechnology and Materials (RONM), National Research and Innovation Agency (BRIN) (No. 4/III.10.5/HK/2024).

CRediT Author Statement

Authors Contributions: Sanji Firmansyah: investigation, formal analysis, writing—original draft preparation. Egi Agustian: Conceptualization, supervision, investigation, formal analysis, writing—review, funding acquisition. Nino Rinaldi: Supervision, interpretation data analysis, and processes. Nuni Widiarti: Supervision, interpretation of data analysis, and processes. Yulizah Hanifah: interpretation data analysis, and processes. Maisaroh: Supervision. Anny Sulaswatty: Supervision, and interpretation of data processes. All authors have read and agreed to the published version of the manuscript.

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