

Synthesis of Sulfated and CaO-Modified UiO-66 Bifunctional Catalysts from Zircon Sand for Conversion of Waste Cooking Oil

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Abstract

Zircon-based UiO-66 metal-organic frameworks (MOFs) were synthesized using zirconium oxychloride extracted from natural zircon sand from Central Kalimantan, Indonesia, and subsequently modified to produce two distinct heterogeneous catalysts for the stepwise conversion of waste cooking oil (WCO) into biodiesel. Sulfated UiO-66 (UiO-66/SO₄) was developed as a solid acid catalyst for the esterification step, while CaO-modified UiO-66 (UiO-66/CaO) was employed as a solid base catalyst for the subsequent transesterification reaction. Structural characterization by XRD and FTIR confirmed the preservation of the UiO-66 framework after functionalization, with successful incorporation of sulfate and calcium species. During esterification process, UiO-66/SO₄ exhibited the highest activity at a catalyst loading of 0.5 wt%, reducing the free fatty acid (FFA) content of WCO by 51.7%. Following this pretreatment, the transesterification step catalyzed by UiO-66/CaO at the same loading yielded the best performance, producing 61.82% biodiesel. The formation of fatty acid methyl esters (FAME) was confirmed by FTIR analysis, showing characteristic ester bands at 1744, 1165, 1031, and 1456 cm⁻¹. These results demonstrate that zircon sand-derived UiO-66 can be effectively tailored into complementary acid and base catalysts, each optimized for a specific reaction step, providing a sustainable and efficient route for biodiesel production from high-FFA waste cooking oil.

Keywords: *Biodiesel, heterogeneous catalyst, UiO-66, waste cooking oil, zircon sand*

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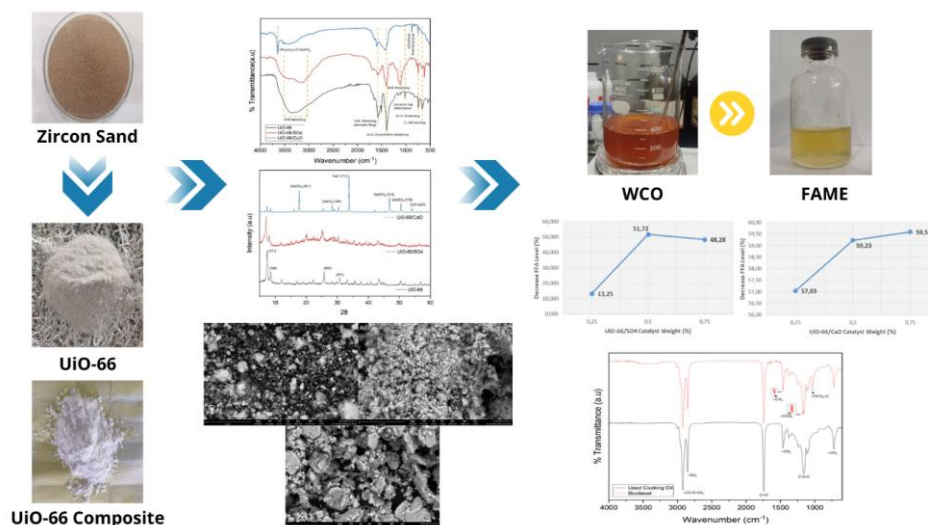
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Graphical Abstract



Introduction

The last two decades have been marked by a tightening global energy landscape, and the pressure to shift away from fossil fuels has never felt more immediate [1]. Among the many alternatives being explored, biodiesel often stands out because it behaves much like regular diesel while carrying the environmental benefits of being biodegradable and producing lower greenhouse gas emissions [2]. Still, producing biodiesel at a competitive price remains a challenge, especially when the feedstock depends on refined vegetable oils. This is one reason waste cooking oil (WCO) keeps attracting attention: it is inexpensive, abundant, and turns what would ordinarily be a disposal problem into a usable fuel source that fits neatly into circular-economy thinking [3].

Processing WCO, however, comes with its own set of complications. The oil often contains a significant amount of free fatty acids (FFAs), and these FFAs have an unfortunate habit of forming soap during alkaline-catalyzed transesterification. Once that happens, the reaction becomes messy—emulsions form, yields drop, and

purification becomes bothersome [4]. A practical workaround is a two-step route: first, an acid-catalyzed esterification to push the FFA level down to safer territory, generally below 2.5%; then a base-catalyzed transesterification to convert the triglycerides into methyl esters [5]. This strategy effectively reduces FFA content prior to transesterification, improving biodiesel yield and product quality. Consequently, the development of heterogeneous acid-base bifunctional catalysts has become a key research focus in biodiesel production from low-quality feedstocks [6].

Zirconia (ZrO_2) frequently appears in these discussions. Its stability—both thermal and mechanical—paired with its intrinsic acid-base character, makes it a versatile option for catalysis [7,8]. Efforts to enhance its surface area and porosity have led to the use of metal-organic frameworks (MOFs) as structural templates, particularly the well-known UiO-66. This zirconium-based MOF is prized for its durability and adjustable pore properties, and when it is calcined, it can transform into a porous form of ZrO_2 that retains much of parent framework's architectural advantages [9]. Previous

studies have shown that UiO-66 can be effectively functionalized to introduce acidic or basic sites for biodiesel-related reactions. For example, sulfonic acid-modified UiO-66 catalysts have achieved fatty acid esterification conversions above 80% under optimized conditions [10].

CaO-based catalysts are widely recognized for their strong basicity and high activity in transesterification reactions; however, their broader application is often constrained by limited stability, catalyst leaching, and poor reusability [11]. To mitigate these shortcomings, recent efforts have focused on immobilizing CaO on zirconium-containing supports. For instance, CaO/ZrO₂ catalysts derived from UiO-66(Zr) have been reported to achieve biodiesel yields of approximately 90% under optimized laboratory conditions, while exhibiting improved structural stability compared to bulk CaO [12]. Despite these advances, most UiO-66-based catalytic systems reported to date still rely on commercially sourced zirconium precursors, which increases production costs and poses challenges for large-scale implementation. Moreover, the direct utilization of locally available zircon-rich minerals as precursors for MOF synthesis remains largely unexplored, even in regions with abundant zircon resources, such as Indonesia [8,13].

In this study, zirconium is sourced not from an imported chemical reagent, but from natural zircon sand found in Central Kalimantan, Indonesia. Although the region is rich in zircon minerals, much of this resource remains underutilized despite its promise as a local precursor for zirconium-based materials [13]. By extracting zirconium oxychloride (ZrOCl₂·8H₂O) directly from the sand, the present work offers a route toward producing UiO-66 that is both economically and geographically advantageous. The synthesized MOF is

subsequently modified in two directions: sulfation to form UiO-66/SO₄ for the esterification step, and incorporation of CaO to generate UiO-66/CaO for the transesterification stage [12,14]. Together, these materials create a bifunctional catalytic system capable of handling high-FFA WCO efficiently, while also demonstrating the broader potential of turning local mineral resources into high-value catalytic materials.

Materials and Methods

Materials and Instrumentations

Natural zircon sand was collected from Kereng Pangi, Pulang Pisau, Central Kalimantan, Indonesia during Juni 2019. Analytical grade chemicals were employed, namely hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH), terephthalic acid (H₂BDC), N,N' Dimethylformamide (DMF), chloroform, methanol, ammonium sulfate ((NH₄)₂SO₄), calcium oxide (CaO), were purchased from Merck Reagent, Germany. Characterization instruments utilized included X-ray diffraction (XRD) (Philips with X'Pert MPD, at room temperature), Scanning Electron Microscopy (SEM) (ThermoFisher Phenom XL G2, magnifications of 350,000x to over 1,000,000x), and Fourier Transform Infrared Spectroscopy (FTIR) (Shimadzu FTIR-8400S spectrometer, signals to noise >55.000:1/min).

Extraction of Zirconium Precursor from Zircon Sand.

The zirconium precursor was extracted from locally sourced zircon sand using an acid leaching technique [15]. The raw zircon sand was first washed, oven-dried, and magnetically separated to eliminate ferromagnetic impurities. The purified material was sieved through a 100-mesh screen to ensure uniform particle size. Subsequently, 6 g of the sieved zircon was

leached in 60 mL of concentrated HCl under continuous stirring at 80 °C for 90 min. The mixture was then filtered, and the clear filtrate obtained was subjected to recrystallization to yield the zirconium precursor ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$).

Synthesis of UiO-66 from Zircon-Derived $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$

UiO-66 was synthesized using a solvothermal approach [16]. A 0.0045 mol solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in 35 mL of DMF (Solution A) and a 0.0045 mol solution of H_2BDC in 35 mL of DMF (Solution B) were prepared separately and stirred for 15 min. Both solutions were then combined and mixed vigorously for 30 min before being transferred into a Teflon-lined autoclave. The sealed reactor was heated at 125 °C for 24 h. The resulting white precipitate was collected and sequentially washed with 30 mL each of DMF, chloroform, and methanol for 12 h per solvent. The purified UiO-66 was dried at 120 °C for 24 h to obtain a fine white powder.

Synthesis of Sulfate-Modified Acid Catalyst (UiO-66/ SO_4)

The acid catalyst (UiO-66/ SO_4) was synthesized via wet impregnation of sulfate ions onto the UiO-66 framework. In a typical procedure, 3 g of UiO-66 was dispersed in 30 mL of 1.5 M ammonium sulfate solution (1:10 w/v) and stirred continuously at room temperature for 24 h. The impregnated solid was then separated, oven-dried at 100 °C for 2 h.

Synthesis of Calcium Oxide-Modified Base Catalyst (UiO-66/ CaO)

The base catalyst (UiO-66/ CaO) was prepared through a hydrothermal impregnation method [17]. UiO-66 (30 wt% relative to CaO) was dispersed in a suspension of 5 g CaO in 50 mL of distilled

water and stirred thoroughly. The mixture was transferred into a Teflon-lined autoclave and treated hydrothermally at 100 °C for 24 h. The obtained solid was then filtered, oven-dried at 105 °C to constant weight.

Esterification of WCO with UiO-66/ SO_4 Catalyst

The esterification process was performed to reduce the free fatty acid (FFA) content of pre-treated waste cooking oil (WCO). The oil was mixed with methanol at a 1:15 molar ratio and refluxed at 45 °C for 10 min [17]. Subsequently, the UiO-66/ SO_4 acid catalyst was introduced at loadings of 0.25, 0.5, and 0.75 wt% relative to the total reactants. The reaction proceeded under reflux at 65 °C for 30 min. After completion, the catalyst was separated, and the esterified oil was collected for FFA determination and subsequent transesterification.

Transesterification of WCO with UiO-66/ CaO Catalyst

The transesterification process was performed using the esterified oil and methanol at a 1:18 molar ratio. The mixture was preheated under reflux at 45 °C for 10 min [17], followed by the addition of the UiO-66/ CaO base catalyst at loadings of 0.25, 0.5, and 0.75 wt%. The reaction proceeded under reflux at 70 °C for 60 min. Afterward, the catalyst was separated, and the upper biodiesel layer was collected and purified for subsequent analysis.

Analytical Methods

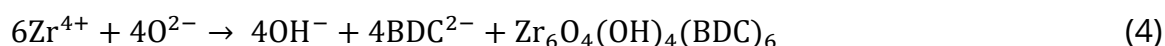
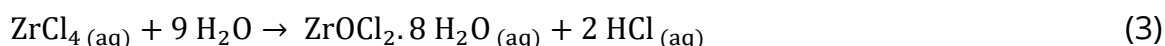
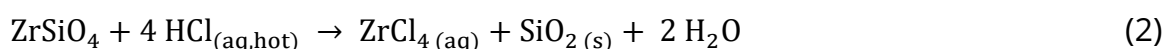
The free fatty acid (FFA) content of both the oil and the produced biodiesel was determined through an acid–base titration method. In this procedure, 1 g of the sample was dissolved in 10 mL of methanol, heated to 45 °C, and titrated with a standardized KOH. The FFA percentage was subsequently calculated based on the molecular weight of

oleic acid (288.45 g/mol) by applying the formula in equation 1[17].

$$\text{FFA content (\%)} = \frac{V_{\text{KOH}} \times N_{\text{KOH}} \times \text{MW}_{\text{KOH}}}{\text{weight of sampel (g)}} \times 100\% \quad (1)$$

The biodiesel yield was determined gravimetrically after catalyst separation and phase purification. The presence of fatty acid methyl esters (FAME) was qualitatively confirmed by FTIR spectroscopy through characteristic ester absorption bands. No chromatographic quantification using external FAME standards was performed in this study.

The functional groups present in both the synthesized catalysts and the produced biodiesel were examined using FTIR spectroscopy (Shimadzu). The crystalline characteristics of the catalytic materials were identified through X-ray diffraction analysis (Bruker D8), and their surface features were further observed using a scanning electron microscope (Thermo Fisher Scientific)



Synthesis of UiO-66

UiO-66 was prepared through a solvothermal reaction using zircon-derived $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and terephthalic acid (H_2BDC). The metal-to-ligand ratio was kept close to 1:1 to help the framework assemble evenly and to reduce coordination defects such as missing linkers [19,20]. When both components were dispersed in DMF, the solvent partially deprotonated H_2BDC , allowing the BDC^{2-} ligand to bind to hydrolyzed Zr^{4+} species. Through gradual hydrolysis and condensation, these

Result and Discussion

Extraction of Zirconium Oxychloride from Zircon Sand

Zirconium oxychloride was extracted from natural zircon sand (ZrSiO_4) through an acid-leaching route. The powdered sand was digested in concentrated HCl at elevated temperature, during which the zircon gradually broke apart and released zirconium species into solution. Once the dissolution reached a steady state, the mixture was filtered to separate remaining silica-rich residues, yielding a zirconium-rich filtrate containing ZrCl_4 species. Subsequent recrystallization of this solution produced zirconium oxychloride octahydrate. The overall transformations occurring during the leaching and precipitation processes are summarized in equation (2) and (3) [8,18].

zirconium units formed $\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters that connected with BDC to generate the UiO-66 framework, as outlined in equation (4) [21].

The solvothermal treatment produced a crystalline 3D porous network in which Zr_6 nodes are linked by aromatic BDC ligands [21]. After synthesis, the solid was washed with DMF, chloroform, and methanol to clear unreacted species, followed by a methanol exchange that opened the pores further [19]. The final product appeared as a fine white crystalline powder (Figure 1a).

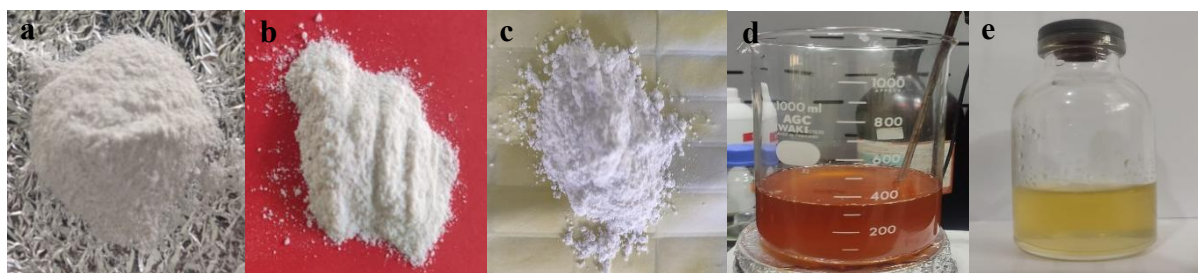


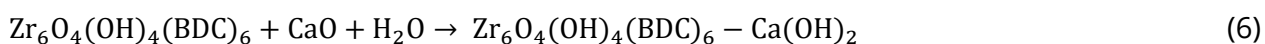
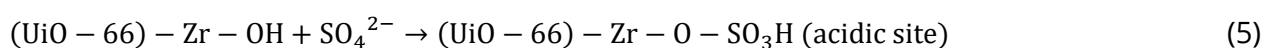
Figure 1. UiO-66 (a); (b) SO₄-Modified UiO-66 (b); (c) CaO-Modified UiO-66; (d) Waste Cooking Oil (WCO); (e) Transesterified Biodiesel

Synthesis of Acidic Sulfate-Modified and Basic CaO-Modified UiO-66 Catalysts

Sulfation was performed to strengthen the acidity of UiO-66 by introducing sulfate ions (SO₄²⁻) into its Zr-based clusters. Sulfate species from ammonium sulfate interacted with Zr-OH groups and Zr-O-Zr linkages on the Zr₆O₄(OH)₄ nodes, forming Zr-O-SO₃H units that contribute both Brønsted and Lewis acidity [9,19]. This interaction, summarized in equation 5 [22], increases the material's acid strength while keeping the original UiO-66 framework intact [23]. The modified UiO-66-SO₄ appeared as a fine white powder (Figure 1b), indicating successful incorporation of sulfate groups

and the creation of an efficient solid acid catalyst for esterification.

For the basic catalyst, UiO-66/CaO was produced through a hydrothermal process designed to merge the structural stability of UiO-66 with the strong basicity of CaO. During synthesis, CaO partially hydrated into Ca(OH)₂, which then formed Ca-O-UiO linkages by interacting with oxygen atoms in the UiO-66 framework [24]. The underlying mechanism is illustrated in Eq. (6) [25]. Some of the CaO dissolved and redeposited within the MOF's pore network under hydrothermal conditions, creating a porous and thermally stable composite while maintaining active CaO sites on the surface [26-28].



Characteristics of UiO-66, SO₄-Modified, and CaO-Modified UiO-66

The FTIR spectra presented in Figure 2 and Table 1 highlight the key vibrational signatures of UiO-66 and its sulfate- and calcium-modified forms. In the unmodified MOF, a broad absorption at 3365 cm⁻¹ reflects O-H stretching from hydroxyl groups within the Zr₆O₄(OH)₄ cluster units

[26]. The bands at 1573 and 1396 cm⁻¹ correspond to the aromatic C=C and asymmetric O-C-O stretching modes of the terephthalate linker, confirming coordination between BDC and the Zr-O nodes [19], [29]. Additional absorptions at 744 and 661 cm⁻¹ assigned to Zr-O bending and stretching signal the presence of well-formed Zr₆ clusters in the framework [10,30].

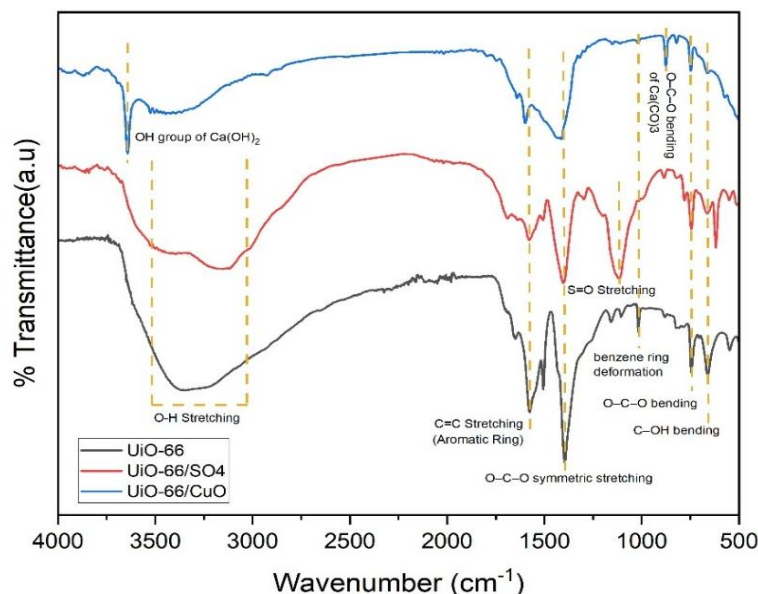


Figure 2. FTIR spectra of UiO-66 MOF, UiO-66/SO₄, and UiO-66/CaO composites

Once sulfate groups were introduced, the spectrum of UiO-66/SO₄ showed a new absorption around 1114 cm⁻¹ of asymmetric S-O stretching. This feature indicates that sulfate species successfully bonded to the zirconium centers, creating stronger Brønsted and Lewis acidic sites [9]. Minor shifts in the carboxylate and aromatic regions also suggest subtle electrostatic interactions, although the integrity of the

organic linker remained intact. The UiO-66/CaO sample displayed two additional bands typical of basic calcium species: an –OH stretching signal at 3664 cm⁻¹ from Ca(OH)₂ and a peak near 874 cm⁻¹ associated with O–C–O bending from CaCO₃. These bands point to the presence of hydrated and carbonated CaO, confirming that calcium species were successfully incorporated onto the UiO-66 architecture [31].

Table 1. Comparative Analysis of FTIR Absorption Bands for Various Materials

FTIR Absorption bands	Wavenumbers (cm ⁻¹)			References
	UiO-66	UiO-66/SO ₄	UiO-66/CaO	
OH group of Ca(OH) ₂	-	-	3664	3640-4642 [31]
O-H stretching	3365	3122	3410	3200-3600 [26]
C=C stretching (Aromatic Ring)	1573	1576	1598	1576 [29]
O–C–O asymmetric stretching	1396	1402	1417	1430 [19]
S-O asymmetric Stretching	-	1114	-	1126 [9]
O–C–O bending of Ca(CO) ₃	874	-	-	872-876 [31]
Zr-O bending	744	745	748	771 [32]
Zr-O Stretching	661	618	662	663 [30]

Figure 3 shows the XRD profiles of UiO-66 and its modified forms, confirming that both sulfation and CaO incorporation altered the framework as intended. The unmodified UiO-66 displays clear peaks at 7.4° , 8.5° , 25.8° , and 30.8° , matching the (111), (200), (600), and (711) planes of its cubic lattice assembled from $\text{Zr}_6\text{O}_4(\text{OH})_4$ nodes and BDC linkers which associated with UiO-66 pattern

(CCDC number 733458) [10,33]. After sulfation, these peaks remain at nearly the same positions but become broader and slightly weaker. This soft decrease in crystallinity suggests that SO_4^{2-} groups created local defects and mild distortions without disrupting the underlying UiO-66 topology [9,23].

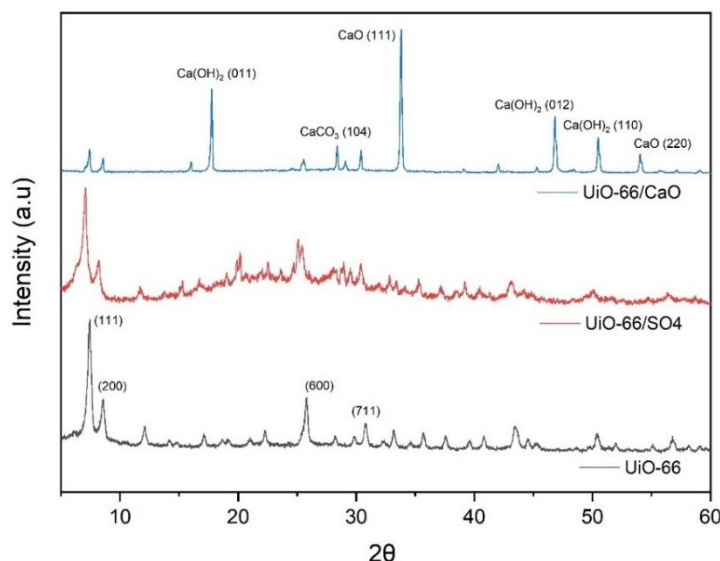


Figure 3. XRD diffractograms of UiO-66 MOF, UiO-66/SO₄, and UiO-66/CaO composites

The diffraction pattern of the UiO-66/CaO composite exhibits additional reflections attributed to calcium-containing phases, with peaks at 33.81° and 54.02° corresponding to cubic CaO (ICCD 00-037-1484), reflections at 17.74° , 46.80° , and 50.47° assigned to $\text{Ca}(\text{OH})_2$ (ICCD 00-044-1481); and a peak at 28.37° associated with rhombohedral CaCO_3 (ICCD 00-003-1123) [17,34]. The presence of these phases partially dampens the characteristic UiO-66 reflections at 7.4° and 8.5° , indicating their contribution to the overall diffractogram. These results indicate that CaO modification leads to the formation of a UiO-66/CaO composite in which the UiO-66 framework remains crystallographically intact, while CaO is present as a physically associated surface phase rather than inducing bulk

structural modification. The minor $\text{Ca}(\text{OH})_2$ and CaCO_3 phases are likely formed during cooling, as CaO encounters trace moisture or CO_2 [26,35]. These phases are predominantly associated with the surface of the UiO-66 framework and do not significantly affect the bulk crystal structure. Subtle shifts in several peaks hint at interactions between Ca^{2+} ions and the UiO-66 carboxylate groups, forming Zr-O-Ca linkages that slightly distort the lattice and strengthen the interface within the composite [36].

The SEM images in Figure 4 show how the morphology of UiO-66 changes after sulfation and CaO loading. The unmodified UiO-66 produced from zircon sand forms submicron polyhedral particles that pack into compact aggregates with smooth faces

and clean edges—a good sign that the Zr-BDC framework crystallized properly. The relatively even particle sizes and the small voids between them suggest controlled nucleation during solvothermal growth, aligning well with earlier descriptions of

highly crystalline UiO-66 exhibiting mild aggregation and good microporosity [20], [37]. This confirms that zircon sand serves as a reliable precursor for generating a stable and porous UiO-66 phase.

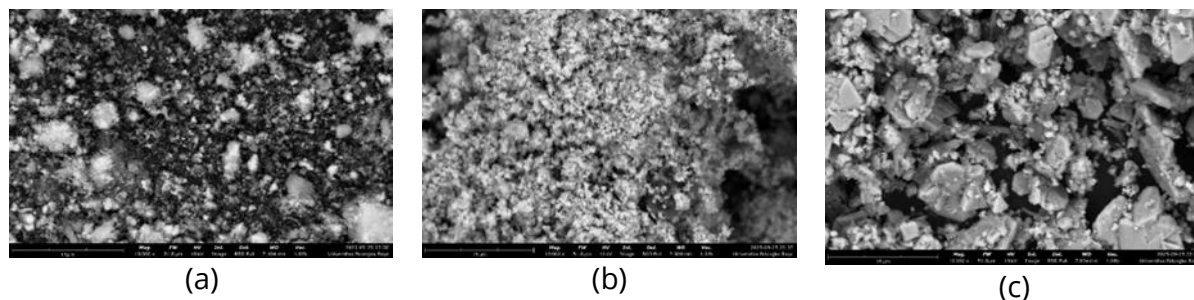


Figure 4. Surface morphology (SEM) of (a) UiO-66 MOF; (b) UiO-66/SO₄, and UiO-66/CaO (c) composite

Once sulfated, the surface of UiO-66/SO₄ becomes noticeably rougher. Wrinkled textures and amorphous patches appear between the crystalline grains, indicating that sulfate groups have interacted with the Zr-O nodes. These local distortions generate additional Brønsted acid sites and open up more accessible surface area, features that tend to enhance molecular diffusion during catalysis [9,23]. In contrast, brighter particles observed in the UiO-66/CaO suggest the presence of Ca-containing species associated with the external surface of the MOF crystallites, although elemental mapping was not performed. Their even dispersion suggests strong interfacial contact with the UiO-66 matrix, creating a composite with both structural stability and pronounced basicity—traits that are advantageous for transesterification in biodiesel synthesis. This morphology mirrors previous reports [12], further indicating that CaO was successfully introduced without undermining the MOF's crystalline backbone.

Esterification of WCO Using UiO-66/SO₄ Catalysts

Figure 5(a) shows a clear drop in the FFA content of waste cooking oil from 1.2547% down to 1.0885%, 0.6057%, and 0.6490% after esterification using UiO-66/SO₄ at loadings of 0.25%, 0.5%, and 0.75%. The 0.5% dosage stands out, achieving a conversion of 51.7%, which seems to strike the right balance between having enough acid sites and keeping the surface open for reactants to reach them. At higher loading, the particles tend to clump together, reducing the amount of accessible active area [38].

The esterification itself proceeds through activation of the fatty acid carbonyl, where -SO₃H Brønsted sites and Zr⁴⁺ Lewis centers work together to increase its electrophilicity, making it easier for methanol to attack and form methyl esters and water [9] as shown in figure 6a. The improved performance at 0.5% likely comes from efficient diffusion through the pores of UiO-66, which allows methanol and fatty acids to interact more freely [17]. Once the loading reaches 0.75%, viscosity and interfacial resistance rise,

slowing mass transfer, while excess sulfate can interfere with Zr-O coordination and narrow the pores [14]. Therefore, 0.5% UiO-66/SO₄ offers the best compromise of

acidity, stability, and diffusivity, giving more than 50% FFA conversion and preparing the oil for transesterification with minimal risk of soap formation [17].

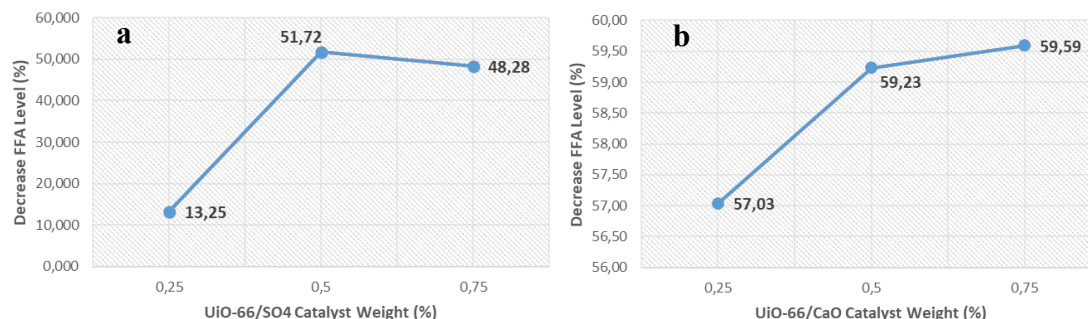


Figure 5. % FFA reduction of WCO versus catalyst weight for the (a) esterification and (b) transesterification reactions.

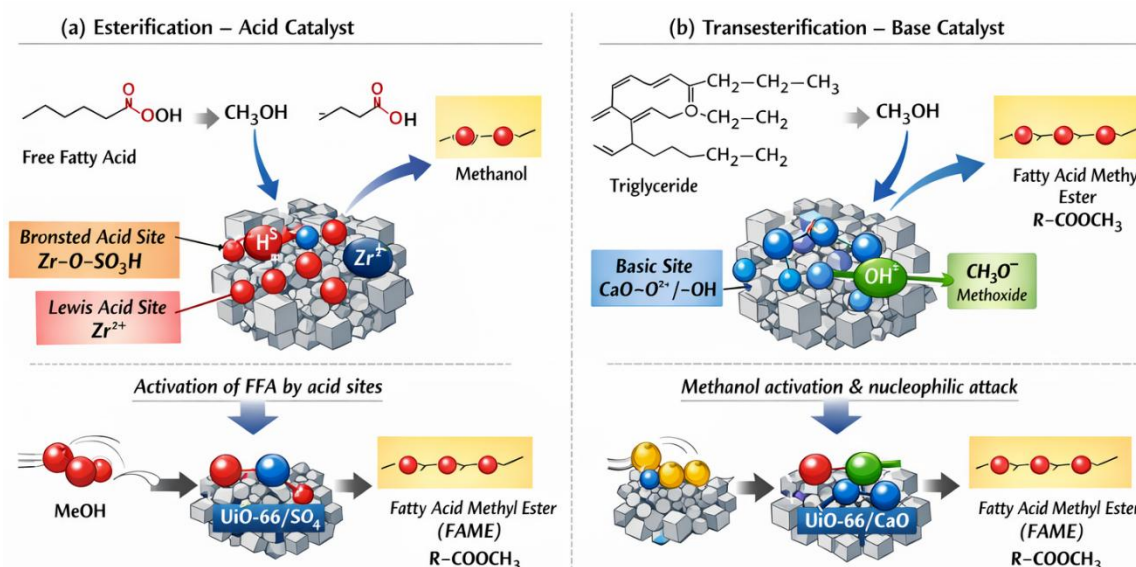


Figure 6. Proposed catalytic mechanism for the esterification and transesterification of waste cooking oil over UiO-66/SO₄ and UiO-66/CaO catalysts.

Transesterification of WCO Using UiO-66/CaO Catalyst

After the transesterification step using UiO-66/CaO, the FFA content in the esterified oil dropped substantially—from 1.2547% to 0.5392%, 0.5115%, and 0.5070% for catalyst loadings of 0.25%, 0.5%, and 0.75%, respectively. These values correspond to FFA reductions of roughly 57–60%, as shown in Figure 5b and Table 2. In contrast, the uncatalyzed reaction produced no biodiesel

under moderate temperatures, consistent with reports that transesterification barely proceeds at moderate conditions [11]. The absence of product is tied to the high energy barrier of methanolysis: without a catalyst or supercritical methanol, methoxide ions simply cannot form in sufficient quantity to attack triglyceride carbonyls [39,40]. Among the tested loadings, the 0.5% catalyst yielded the highest biodiesel content at 61.82%. Increasing the loading to 0.75% reduced the

yield to 53.64%, likely due to increased viscosity and poorer methanol diffusion [17], [29]. For comparison, bulk CaO catalysts can reach biodiesel yields of about 80% under optimized conditions, as reported by [41] snail shell-derived CaO applied to waste cooking oil. The lower yield obtained in this study likely reflects differences in catalyst structure, feedstock quality, and reaction conditions. The basic -O^{2-} and -OH sites on CaO, supported by the UiO-66 framework, facilitate methanol deprotonation to methoxide an essential nucleophile that converts triglycerides into methyl esters and glycerol [12] as shown in figure 6b.

The strong performance at 0.5% suggests a good balance between available basic sites and efficient reactant transport through the porous UiO-66 structure. The uniform CaO dispersion improves surface contact and adsorption, while Zr-O-Ca interactions help

maintain structural robustness during reaction [14], [17]. At higher loadings, particle aggregation and partial pore blockage reduce surface accessibility and hamper conversion [19]. Overall, UiO-66/CaO at 0.5% offers an effective combination of basicity, stability, and diffusion pathways for biodiesel production, as illustrated in Figure 1e.

Table 2. Biodiesel Yield with Variation of Basic Catalyst Mass

Catalyst	Yield (%)
Uncatalyzed	- [11]
UiO-66/CaO 0.25 % wt	56.91
UiO-66/CaO 0.50 % wt	61.82
UiO-66/CaO 0.75 % wt	53.64

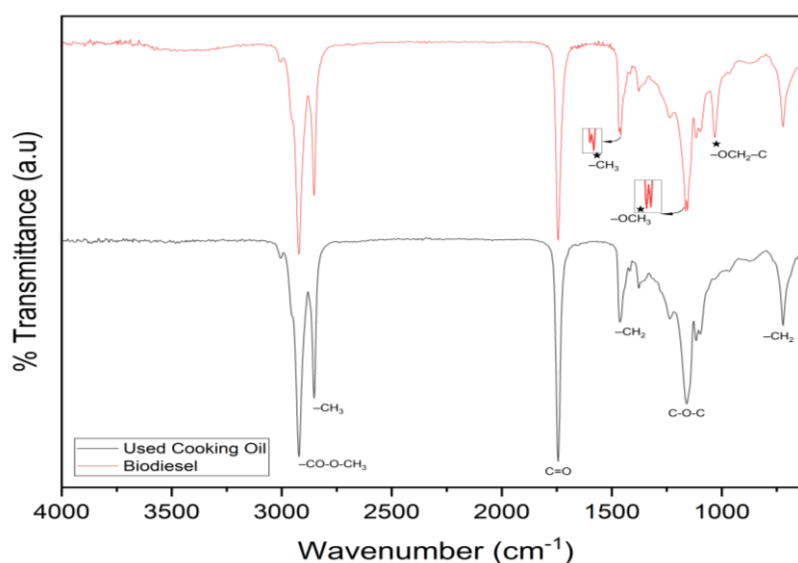


Figure 7. FTIR spectra of waste cooking oil and the produced biodiesel.

The FTIR spectra in Figure 7 clearly indicate that the waste cooking oil was successfully converted into biodiesel. In the original WCO spectrum, the strong carbonyl band at 1743 cm^{-1} typical of triglycerides appears alongside methylene C-H stretches at 2921 and 2853

cm^{-1} [42]. After transesterification, new absorptions emerge at 1165 and 1031 cm^{-1} , which correspond to C-O stretching in -OCH_3 and $\text{-OCH}_2\text{-C}$ groups, confirming the formation of methyl esters [31]. The carbonyl peak near 1744 cm^{-1} remains visible, signaling the presence of ester

functionalities, while the disappearance of the 1157 cm^{-1} glycerol band reflects the breakdown of triglycerides [43].

A distinct band at 1456 cm^{-1} , associated with CH_3 bending of $-\text{CO}-\text{O}-\text{CH}_3$, provides additional evidence of FAME formation [17]. Meanwhile, the persistent peak at 721 cm^{-1} linked to long chain $-\text{CH}_2-$ bending indicates that the fatty acid chains remain structurally intact [44]. Together, the features at 1165, 1031, and 1456 cm^{-1} act as reliable diagnostic fingerprints for successful biodiesel production [31].

Conclusions

This work shows that zircon sand can be turned into a reliable precursor for producing UiO-66 and its bifunctional variants, which perform well as catalysts for converting waste cooking oil into biodiesel. The solvothermal synthesis produced a stable UiO-66 framework, and its subsequent modification with sulfate and CaO successfully generated acid and base catalytic sites. XRD patterns retained the hallmark UiO-66 peaks at $2\theta = 7.4^\circ, 8.5^\circ, 25.8^\circ$, and 30.8° , while additional reflections at 33.8° and 54.0° confirmed CaO formation. FTIR signals at 1114 cm^{-1} (S-O), 3664 cm^{-1} (O-H from $\text{Ca}(\text{OH})_2$), and 874 cm^{-1} (O-C-O of CaCO_2) further verified the surface functionalization. Catalytic tests revealed that 0.5 wt% UiO-66/ SO_4 was the most efficient for esterification, lowering FFA from 1.2547% to 0.6057% (51.7% conversion). The subsequent transesterification step using 0.5 wt% UiO-66/CaO reduced the FFA level to 0.5115% and delivered a biodiesel yield of 61.82%. FTIR analysis of the final product showed clear ester signatures at 1744, 1165, 1031, and 1456 cm^{-1} , confirming the formation of fatty acid methyl esters. Overall, the bifunctional UiO-66/ SO_4 and UiO-66/CaO catalysts offer a promising route

for upgrading low-quality feedstocks into biodiesel with good conversion efficiency.

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Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Ethical Standards

This article does not contain any studies involving human or animal subjects.

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