Automotive Experiences
Vol. 5 No. 2 (2022) pp. 217-229
p-ISSN: 2615-6202 e-ISSN: 2615-6636

Research Paper

Selectivity of the New Catalyst ZnO-MCM-48-CaO in Esterification of *Calophyllum inophyllum* Oil

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https://doi.org/10.31603/ae.6711

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Published by Automotive Laboratory of Universitas Muhammadiyah Magelang collaboration with Association of Indonesian Vocational Educators (AIVE)

Article Info
Submitted:
27/02/2022
Revised:
01/04/2022
Accepted:
06/04/2022
Online first:
18/04/2022

Abstract

The synthesis of MCM-48 containing surfactants (CTAB and Triton X-100), ZnO, and CaO aimed to find a potential heterogeneous catalyst in the esterification of *Calophyllum inophyllum* oil to biodiesel. This research is important in the production of biodiesel from vegetable oils with more than 2% free fatty acids (FFA), such as *Calophyllum inophyllum* oil using heterogeneous catalysts. Synthesis of heterogeneous catalysts, MCM-48 and ZnO-MCM-48-CaO (ZMC), using the hydrothermal method at various calcination temperatures was conducted to find the optimum calcination temperature for the reaction. The activity of the catalyst in the reaction was determined using acid-base titration methods and GC-MS. The MCM-48 catalyst calcined at 650 °C (MCM-48/650) had a catalytic activity of 35.74% and was selective for converting linoleic acid in *Calophyllum inophyllum* oil to biodiesel. In addition, this catalyst was also capable of cracking the compounds contained in *Calophyllum inophyllum* oil into suitable hydrocarbons for biodiesel. In the esterification of vegetable oils, four heterogeneous catalysts (MCM-48/550, ZMC/550, ZMC/650, and ZMC/750) had the potential to replace conventional catalysts (H_2SO_4), particularly in the generation of biodiesel from *Calophyllum inophyllum* oil.

Keywords: Free fatty acid; Heterogeneous catalyst; Mesoporous silica; Brønsted acid; Silanol

1. Introduction

Fossil fuels as an energy source play an essential role in human survival. However, fossil fuels are non-renewable sources of fuel. Therefore, excessive and prolonged exploration results in the reduction of these energy sources [1]. Scientists have made various efforts to overcome this problem by looking for alternative energy sources such as geothermal energy [2], solar energy [3], biogas [4], bioethanol [5], and biodiesel [6]. Among these alternative energy sources, biodiesel is a promising energy source because it is easy to produce, use, and develop [1], [7]. One of the potential sources of biodiesel is biodiesel *Calophyllum inophyllum* oil. This plant grows naturally and is widespread globally [8]. In Indonesia, this plant is commonly found on the coast, easy to grow again, non-edible, the seeds have a high oil content (75%) [9], [10], and produce fruit throughout the year [11]. Therefore, the plant is suitable to be used as a biodiesel feedstock [12].

The high content of FFA in *Calophyllum inophyllum* oil is an obstacle to biodiesel production [13]. Although researchers prefer to use homogeneous acid catalysts in esterification to overcome this problem [14], this method is not environmentally friendly [15]. The catalyst is difficult to be separated from the product at the end of the reaction [16] and is not reusable [17]. Furthermore, the method is not economical [18], [19]. Heterogeneous catalysts can overcome these problems [20], [21].

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Nomenclature

CaAc/600	Calcium acetate hydrate calcined at 600 °C
CaAc	Calcium acetate hydrate ($Ca(CH_3COO)_2.xH_2O$)
ZnAc/650	Zinc acetate dihydrate calcined at 650 °C
ZnAc	Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$)
CTAB	Cetyl trimethyl ammonium bromide

Several studies used heterogeneous catalysts in the esterification of *Calophyllum inophyllum* oil. The catalysts were β-zeolite modified by phosphoric acid [22], sulfonated microcrystalline carbon cellulose [23], MCM-48-CaO [24], Al-MCM-41 [25], and Al/Fe-graphite oxide [26]. According to research, the Al-MCM-41 catalyst provides the highest conversion rate (up to 98%). By adding aluminum to MCM-41, the catalyst's Lewis and Bronsted acid sites were enhanced, resulting in higher activity [27], [28]. Unfortunately, the method offered by this catalyst is not cost-effective (reaction time was 5 hour). Increasing the activity of the mesoporous silica catalyst in the reaction can be carried out by adding hetero-metals [29].

Hetero-metals can generate acid and base sites (bifunctionality) to catalyze esterification and transesterification simultaneously. Several studies used this bifunctional catalyst. The SrO–ZnO/Al_2O_3 catalyst was able to convert 96% of used cooking oil (18 wt% FFA) into biodiesel [30]. The CaO-ZnO catalyst converted 96% Karanja oil (9 wt% FFA) into biodiesel and is more active than MnO_2-CaO, Fe_2O_3-CaO, Fe_2O_3/CaO, Al_2O_3/CaO, and CaO catalysts in the reaction [31]. The W/Ti/SiO_2 catalyst was able to convert 98% used cooking oil (3 wt% FFA) into biodiesel [32]. The use of the catalysts reported were also uneconomical because the reaction took a long time and used a high amount of methanol. However, when applied to *Calophyllum inophyllum* oil with high level of FFA, the activity of the CaO-ZnO catalyst in esterification was better than other catalysts.

Another study also proved that heterogeneous catalyst, KIT-6, [33] was more active than MCM-41 in esterification reactions of vegetable oils. Similar to KIT-6, MCM-48 also has a three-dimensional pore structure so that the possibility of pore-clogging can be avoided [34], [35]. Other studies reported that the presence of surfactants (CTAB and Triton X-100) can increase the activity of mesoporous silica catalysts in simultaneous conversion processes of biodiesel [36]–[38]. Therefore, in this study, a new heterogeneous catalyst consisting of surfactant, MCM-48, ZnO, and CaO was prepared. This study aims to find a potential heterogeneous catalyst in the esterification reaction of *Calophyllum inophyllum* oil to biodiesel.

2. Materials and Methods

2.1. *Materials*

Sample *Calophyllum inophyllum* was obtained from Kalauli Hamlet, Leihitu District, Central Maluku Regency, Maluku Province, Indonesia. Phenolphthalein, $Ca(CH_3COO)_2.xH_2O$, $Zn(CH_3COO)_2.2H_2O$, NaOH, CH_3COOH, *n*-hexane, methanol, and H_3PO_4 were from Merck. While Ludox HS40, CTAB, and Triton X-I00 were from Sigma Aldrich (all chemicals were purchased in pro analysis grades).

2.2. *Calophyllum inophyllum oil*

Modifying the procedure reported in reference [39] was done for degumming *Calophyllum inophyllum* oil. Extraction of *Calophyllum inophyllum* seed oil used *n*-hexane solvent in a soxhlet apparatus. After the extraction, the oil was separated from the solvent using a rotary evaporator. The extracted oil was then heated in an oven for 60 minutes at 105 °C [40].

2.3. *Degumming*

The degumming procedure of *Calophyllum inophyllum* oil used the procedure given elsewhere [41]. *Calophyllum inophyllum* oil was put into a beaker and heated to 65 °C. After that, 5% (v/v) H_3PO_4 was added to the oil while stirring at 1000 rpm for 1 hour at 65 °C. Furthermore, the mixture was allowed to stand for 12 hours, then decanted. The oil obtained was then washed on a separatory funnel using hot distilled water (60-80 °C) until the pH of the wastewater from the washing process was neutral. The oil layer was then heated in the oven for 60 minutes at 105 °C. The FFA content of the oil obtained was then determined [42].

2.4. *Synthesis and characterization of catalysts*

The procedures reported in reference [43] were modified to synthesize ZMC catalysts. In the silica source, $Zn(CH_3COO)_2.2H_2O$ and $Ca(CH_3COO)_2.xH_2O$ were added as precursors to ZnO and CaO, respectively. The composition of

ZnO and CaO in MCM-48 was 1: 1 (n/n). As-synthesized catalysts (CTAB-MCM-48 and CTAB-ZMC) and calcined for 5 *hour* at temperatures of 550 °C (MCM/550 and ZMC/550), 650 °C (MCM/650 and ZMC/650), and 750 °C (MCM/750 and ZMC/750). FTIR (Shimadzu 8300) was used to detect the presence of surfactants in the MCM-48 catalyst. The success of catalyst synthesis was confirmed by X-ray diffraction (XRD). XRD data for powder samples were collected using Cu Kα radiation (λ = 0.154 nm) in the 2θ range of 2–80° at the scanning speed of 2 °/min. Diffraction patterns were compared to references and ICDD (International Centre for Data Diffraction) data to identify the catalysts. XRF (Panalytical, Minipal 4) was used to identify metal oxides (CaO and ZnO) in the CTAB-ZMC catalyst.

2.5. *Esterification*

The esterification of *Calophyllum inophyllum* oil on accomplished using the procedure described in elsewhere [44]. Esterification took place in a 100 mL three-neck flask equipped with an electric heater, a thermometer, a magnetic stirrer, and a cooler. The reaction temperature was maintained at 62 °C with a stirring rate of 1200 rpm, a 2%-wt/wt catalyst to methanol, while the ratio of oil to methanol was 1:9 (wt/wt) reaction time was 1 *hour*. The reaction was halted by submerging the three-neck flask in an ice chiller. Then the mixture was filtered through a Buchner funnel using filter paper. The levels of FFA in the product were then determined using the acid-base titration technique [23]. The best conversion results were also identified using the GC-MS method (QP 2010 Ultra Shimadzu).

3. Results and Discussion

3.1. *Characterization of MCM-48 and ZMC Catalysts*

The XRD patterns show the success in the preparation of as-synthesized and calcined MCM-48 (**Figure 1**). There is a moderate intensity peak at 2.51° 2θ observed in the XRD pattern of CTAB-MCM-48 (**Figure 1a**). This peak is a characteristic of MCM-48 containing surfactant [45].

The XRD pattern of MCM-48/550 (**Figure 1b**) shows a strong peak on 2.61° 2θ and several low peaks on 4.0-5.0° 2θ (4.33, 4.48, 4.52, 4 .59, and 4.68°). These peaks are specific characteristics of the three-dimensional structure of the MCM-48 catalyst after the loss of surfactant [43]. The calcination temperature of 650 °C for the MCM-48/650 catalyst improved its three-dimensional structure with increasingly intensity of (**Figure 1c**) peaks in the 4.0-5.0° 2θ region (4.37, 4.41, 4.44, 4.48, 4.51, 4.58, and 4.62°) [46]. The use of a calcination temperature of 750 °C revealed that the three-dimensional structure of the MCM-48/750 catalyst began to deteriorate (**Figure 1d**) [47]. The damage to the catalyst structure occurs caused by the calcination temperature exceeding the thermal conditions of the MCM-48 [48].

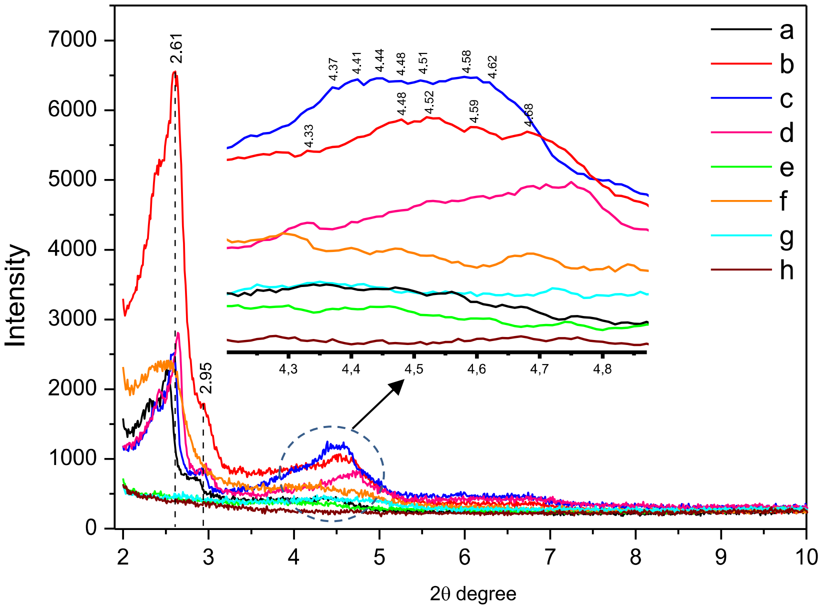
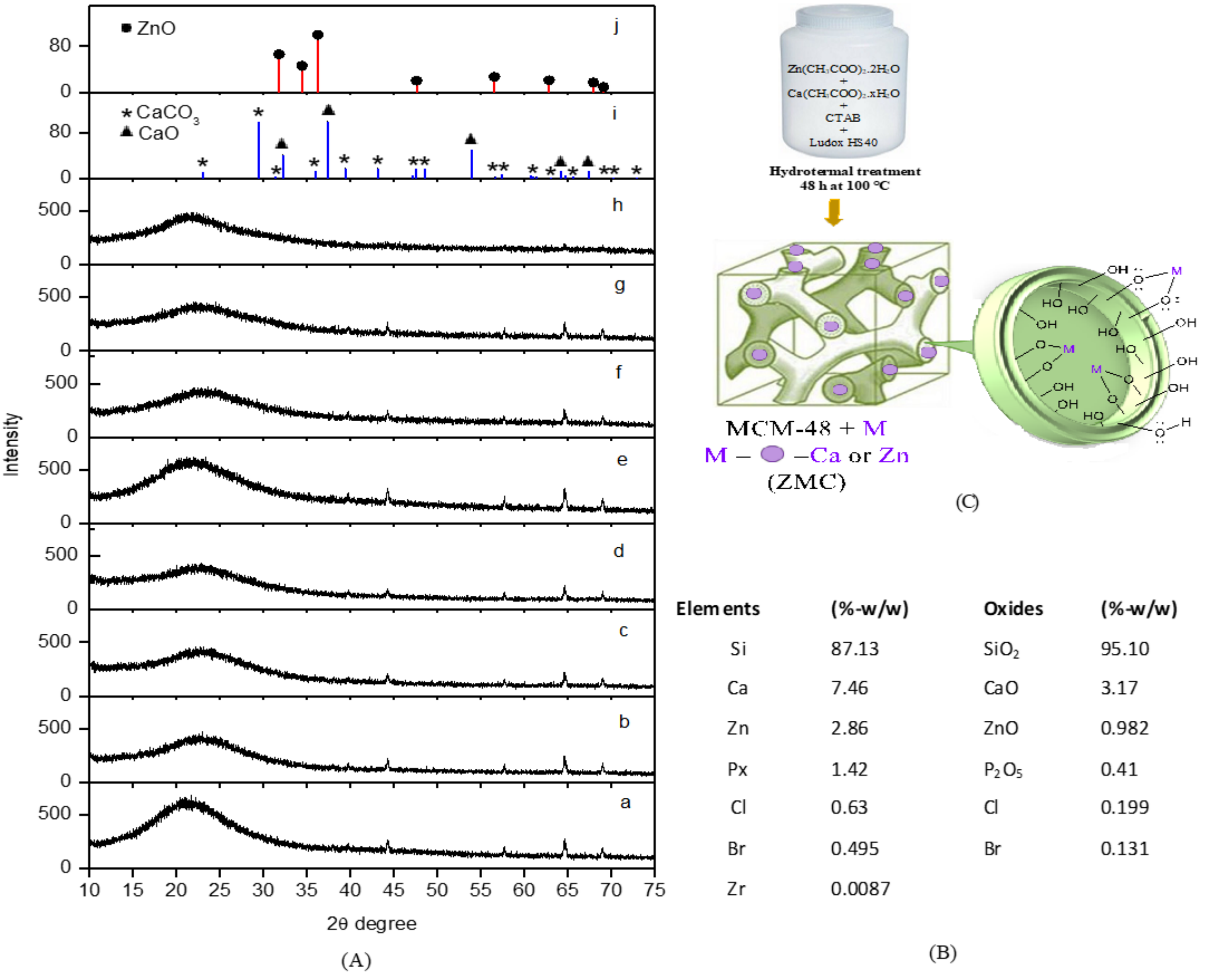


Figure 1. X-ray diffraction patterns of; a) CTAB-MCM-48, b) MCM-48/550, c) MCM-48/650, d) MCM-48/750, e) CTAB-ZMC, f) ZMC/550, g) ZMC/650, and h) ZMC/750



Elements	(%-w/w)	Oxides	(%-w/w)
Si	87.13	SiO_2	95.10
Ca	7.46	CaO	3.17
Zn	2.86	ZnO	0.982
Px	1.42	P_2O_5	0.41
Cl	0.63	Cl	0.199
Br	0.495	Br	0.131
Zr	0.0087		

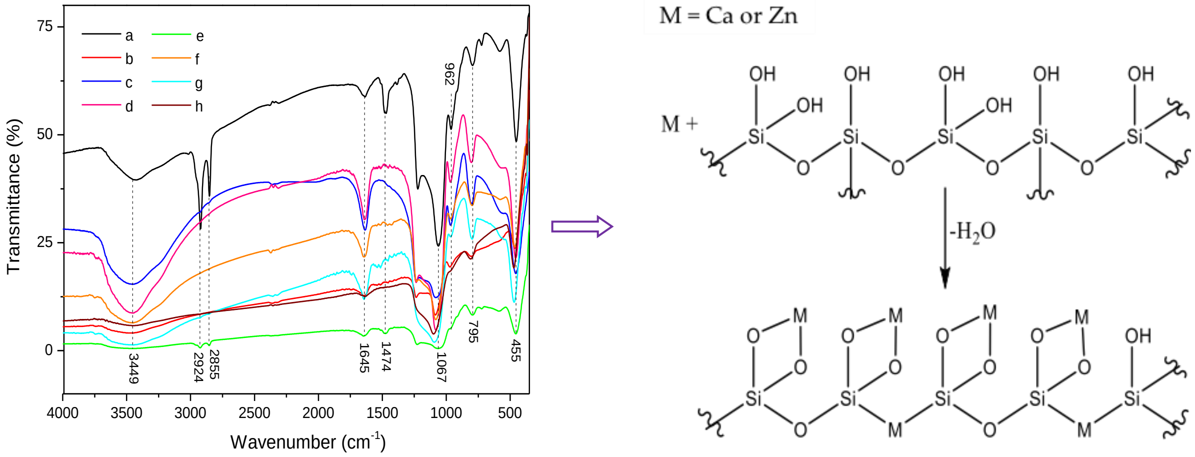
Figure 2. A) X-ray diffraction patterns for wide-angle 2 theta of a) CTAB-MCM-48, b) MCM-48/550, c) MCM-48/650, d) MCM-48/750, e) CTAB-ZMC, f) ZMC/550, g) ZMC/650, and h) ZMC/750, i) CaAc/600 (ICDD $CaCO_3$: 00-005-0586 and CaO: 04-003-7161), j) ZnAc/650 [49], B) Composition of chemical elements contained in CTAB-ZMC, and C) Reaction of CaO and ZnO in the three-dimensional channel MCM-48

The addition of CaO and ZnO into MCM-48 destroyed the three-dimensional shape of MCM-48. Shift, decrease in intensity (**Figure 1f**), and loss of peaks typical for the three-dimensional structure of MCM-48 (**Figure 1 e**, **g**, and **h**) confirmed that matter. These characters indicate that CaO and ZnO have reacted with silanol (Si-OH) and siloxane (Si-O-Si) groups in the MCM-48 three-dimensional channel to form Si-O-Ca or Si-O-Zn (**Figure 2C**). The occurrence of the reaction in the three-dimensional MCM-48 channel confirmed by the results of XRF analysis (**Figure 2B**) and the XRD pattern for the wide-angle 2 theta of the ZMC catalyst (**Figure 2A**) did not show X-ray diffraction peaks for CaO and ZnO [50].

Figure 3A depicts the FTIR spectra of as-synthesized and calcined catalysts, with interpretation findings in **Table 1**. The loss of surfactant from the catalyst was confirmed by the FTIR analysis (**Figure 3 b**, **c**, and **d**), which revealed the loss of peaks for CH stretching vibration (2853 cm^{-1} and 2922 cm^{-1}) and CH bending (1470 cm^{-1}) from the CH_3 groups, as well as the shift of the stretching vibration peak siloxane to a larger wavenumber. The same thing happened for the CTAB-ZMC catalyst to ZMC [51], [52]. The interaction of CaO and ZnO with the silanol group of MCM-48 was supported by the findings of FTIR analysis, which revealed a drop in intensity and a shift in peaks silanol group absorption [24], [53]. In addition, the bending and stretching vibration peaks of siloxane also shifted to a higher wavenumber after the addition of ZnAc and CaAc. The reaction of ZnO and CaO with siloxane groups on the silica framework to form Si-O-Zn or Si-O-Ca confirms that matter [53], [54]. The proposed mechanism of CaO and ZnO reaction with silanol and siloxane in MCM-48 is shown in **Figure 3B**.

Table 1. FTIR analysis of synthesized catalyst

Catalyst	Group	Wavenumber (cm^{-1})	
		This Work	**Reference**
CTAB-MCM-48	Silanol	3426 and 1638	[55]
	Siloxane	1223, 1063, 795, 453	[56]
MCM-48/550	Silanol	3480 and 1644	[57]
	Siloxane	1086, 804 and 465	[58]
MCM-48/650	Silanol	3451 and 1636	[59]
	Siloxane	1082, 802, and 455	[59]
MCM-48/750	Silanol	3451 and 1641	[60]
	Siloxane	1082, 804, and 455	[59]
CTAB-ZMC	Silanol groups absorption overlaps with Si-O-Ca or Si-O-Zn groups absorption	3449 and 1645	[24]
	Siloxane group absorption overlaps with Si-O-Ca or Si-O-Zn group absorption	1227, 1067, 795 and 455	[60]
ZMC/550	Silanol groups absorption overlaps with Si-O-Ca or Si-O-Zn groups absorption	3451 and 1643	[24]
	Siloxane group absorption overlaps with Si-O-Ca or Si-O-Zn group absorption	1082, 798 and 463	[24]
ZMC/650	Silanol groups absorption overlaps with Si-O-Ca or Si-O-Zn groups absorption	3449 and 1643	[61]
	Siloxane group absorption overlaps with Si-O-Ca or Si-O-Zn group absorption	1094, 798 and 469	[62]
ZMC/750	Silanol groups absorption overlaps with Si-O-Ca or Si-O-Zn groups absorption	3443 and 1641	[63]
	Siloxane group absorption overlaps with Si-O-Ca or Si-O-Zn group absorption	1099, 810 and 471	[63]



(A) (B)

Figure 3. A) FTIR Spectrum of a) CTAB-MCM-48, b) MCM-48/550, c) MCM-48/650, d) MCM-48/750, e) CTAB-ZMC, f) ZMC/550, g) ZMC/650, h) ZMC/750; and B) reaction mechanism of CaO and ZnO with silica in MCM-48

3.2. *Catalytic Activity*

In the esterification of *Calophyllum inophyllum* oil, CTAB-MCM-48 and CTAB-ZMC catalysts displayed lower activity than MCM-48 and ZMC catalysts (**Figure 5**). The poor activity of the catalyst is due to the surfactant's head (hydrophilic) and tail (hydrophobic) structures, which can deactivate the active group of FFA, causing the yield to mix with water and glycerol as a by-product of the reaction, lowering the reaction yield [64]. The effect of surfactants in the CTAB-MCM-48 and CTAB-ZMC catalysts is shown in **Figure 4**.

Figure 5 compares the catalytic activity of the synthesized catalyst to conventional catalyst in the esterification of *Calophyllum inophyllum* oil. This catalytic activity indicates that the higher the absorption intensity of the silanol group, the higher the activity of MCM-48 and ZMC catalysts. Despite having a higher silanol groups absorption intensity than all other catalysts, the three-dimensional structure of the MCM-48/750 catalyst has been damaged. The damage of the three-dimensional structure reduces the surface area of MCM-48/750, resulting in a lower activity of MCM-48/750 compared to that of MCM-48/650.

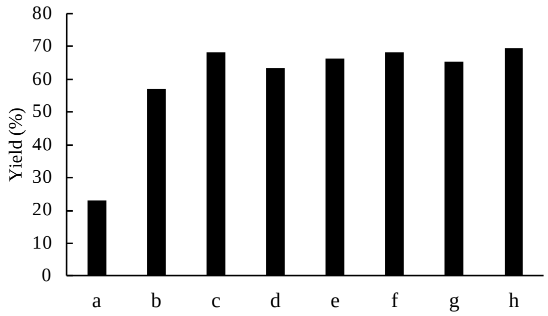


Figure 4. Profile of the effect of surfactants in the catalyst; a) CTAB-MCM-48, b) MCM-48/550, c) MCM-48/650, d) MCM-48/750, e) CTAB-ZMC, f) ZMC/550, g) ZMC/650, and h) ZMC/750 in the esterification

The addition of ZnO and CaO to MCM-48 also decreased the activity of ZMC catalyst in the esterification of *Calophyllum inophyllum* oil. Partially occluded pores with ZnO and CaO induced a decrease in the catalytic activity. However, the presence of these two metal oxides increased the thermal stability of the ZMC catalyst. The breakthrough provides a great starting point for using a catalyst in the same process, particularly in the high-temperature synthesis of biodiesel from *Calophyllum inophyllum* oil. The optimal calcination temperature for MCM-48 was 650 °C, whereas the ZMC catalyst was 550 °C (**Figure 5**). The FTIR spectrum reveals that the silanol groups, as Bronsted acid, act as the catalyst's active site [65], [66]. In addition, the surface area of the catalyst also affects its activity in esterification.

The results characterized using GC-MS (**Table 2**) show that–MCM-48/650 can convert FFA of *Calophyllum inophyllum* oil (**Table 2B**) but it is more specific for converting linoleic fatty acids into biodiesel. In addition, this catalyst also has the activity to crack the components of the compounds contained in *Calophyllum inophyllum* oil into hydrocarbons (**Table 2A**). Therefore, it is suitable for producing biodiesel [67], [68].

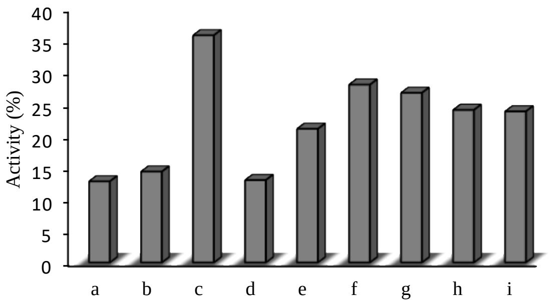


Figure 5. Catalytic activity; a) CTAB-MCM-48, b) MCM-48/550, c) MCM-48/650, d) MCM-48/750, e) CTAB-ZMC, f) ZMC/550, g) ZMC/650, h) ZMC/750, and i. H_2SO_4 in the esterification

Table 2. MCM-48/650 catalytic activity in *Calophyllum inophyllum* oil esterification

Catalysts	**A**				**B**				
	Hydrocarbons				**Fatty Acids**				
	SI (R.T)	**Compounds©**	**C**	**D¥ (%)**	**Acid¥ (%)**	**SI**	**Compounds©**	**Esters¥ (%)**	**SI**
B.E®	95(27.62) and 88(31.76)	Tetradecanal	14	0.01 and 0.24	8.64 21.95	94 92	Palmitic Linoleic		
	85	14-Methyl-8-hexadecyn-1-ol	17	0.19	4.23	95	Oleic		
	87	1-Nonadecene	19	0.03	3.44	90	Stearic		
	90	2-(9-octadecenyloxy)-Ethanol	20	0.32					
	89	9-Eicosyne	20	0.47					
	85	2-mono-Linolein	21	0.37					
	85	di-(9-Octadecenoyl)-Glycerol	39	19.97					
	87	2-mono-Olein	21	2.88					
	93	1-Tricosene	23	0.29					
	87	9,12-Octadecadien-1-ol	18	0.10					

Catalysts	A				B				
	Hydrocarbons				Fatty Acids				
	SI (R.T)	Compounds©	C	D¥ (%)	Acid¥ (%)	SI	Compounds©	Esters¥ (%)	SI
MCM-48/650	94	1,3-p-Menthadiene#	10	0.31	12.42	94	Palmitic	0.84 0.41*	96 97
	96	Furan, tetrahydro-2,2-dimethyl-5-(1-methyl-1-propenyl)#	10	0.22			Linoleic	0.76 29.01	96 87
	95	1,4-Cyclohexadiene, 1-methyl-4-(1-methylethyl)#	10	0.25	20.48	95	Oleic	1.42	95
	95	2-Carene#	10	0.45	5.30	95	Stearic	1.30 0.24*	95 96
	96	Cyclohexene, 1-methyl-4-(1-methylethylidene)#	10	0.61					
	96(10.49) and 95(11.42)	1,2,4,5-Tetramethylbenzene$	10	0.21 and 0.43					
	89	1,1,3,3-tetramethoxypropane	7	0.19					
	97	2,4-Decadienal	10	0.52					
	85	1H-3a,7-Methanoazulene, 2,3,6,7,8,8a-hexahydro-1,4,9,9-tetramethyl-, (1α,3a.α,7α,8a.β)#	15	0.52					
	86	Tricyclo[4.3.0.0(7,9)]non-3-ene, 2,2,5,5,8,8-hexamethyl-(1α, 6β, 7α, 9α)#	15	0.24					
	86	Longifolene#	15	0.29					
	86	3,4,5-Trimethylphenol$	9	2.67					
	86	Cedrene-V6#	15	1.78					
	88(17.85) and 89(19.19)	α-Chamigrene#	15	0.46 and 0.38					
	98	Pentadecane	15	0.23					
	97	Oktadecane	18	0.29					
	97	Nonadecane	19	0.29					
	94	2-Nonadecanone	19	0.29					
	97(35.43) and 94(40.29)	Docosane	22	0.27 and 0.28					
	97(31.82), 97(37.11) and 97(38.73)	Eicosane	20	0.27, 0.36 and 0.27					
	88	9,12-Octadecadienoic acid (Z,Z)-, 2-hydroxy-1-(hydroxymethyl)ethyl ester	21	0.89					
	87	di-(9-Octadecenoyl)-Glycerol	39	1.41					
	97	1-Hexadecene	16	0.43					
	93	Squalene	30	1.25					

Table 3. Comparison of synthesized catalytic activity with previous studies

Catalyst	Esterification-transesterification						Reference
	Methanol: Oil (n/n)	Temperature (°C)	Time (h)	FFA (%)	Feedstock	Conversion (%)	
W/Ti/SiO_2	30:1	65	4	3	Waste oil	98	[32]
	30:1	65	4	8	Waste oil	49	[32]
ZnO-CaO	12:1	65	1	6	Jatropha	98	[31]
	12:1	65	1.5	9	Karanja	96	[31]
Al-MCM-41	3:1	60	5	10	*Calophyllum inophyllum*	98	[25]
ZMC/550	9:1$^{\$}$	62	1	20*	*Calophyllum inophyllum*	41*	This work
MCM-48/650	9:1$^{\$}$	62	1	20*	*Calophyllum inophyllum*	52*	This work
	9: 1$^{\$}$	62	1	22$^{\#}$	*Calophyllum inophyllum*	100$^{@}$	This work

h (hour), n (molar), $^{\$}$wt/wt, *Acid-base titration, $^{\#}$Linoleic acid (GC-MS), $^{@}$linoleic acid methyl ester (GC-MS)

Table 3 shows that increasing the FFA content of vegetable oils can decrease the activity of the catalyst in the reaction. This finding shows that the catalysts synthesized in this study (ZMC/550 and MCM-48/650) have better activity than the catalysts in the literature, especially Al-MCM-41 in the esterification of *Calophyllum inophyllum* oil.

4. Conclusion

The addition of CaO and ZnO into MCM-48 caused the damage of the three-dimensional structure of the ZMC catalyst. The hydrophobic and hydrophilic sides of the surfactant decreased the catalytic activity. The Brønsted acid site of the silanol group and the surface area of the catalyst were the active sites of the catalyst that play a role in this reaction. The synthesized catalyst has higher activity than conventional catalysts in the reaction. In addition to provide the best activity in the reaction, MCM/650 catalyst was also selective for converting linoleic acid into biodiesel. Furthermore, this catalyst was also capable of cracking the compounds contained in *Calophyllum inophyllum* oil to make it suitable for biodiesel. The successful synthesis of this heterogeneous catalyst provides an opportunity to simplify the reaction system and minimize environmental hazards arising from conventional catalysts in the biodiesel production process from vegetable oils, particularly *Calophyllum inophyllum* oil.

Acknowledgement

The author would like to thank the Directorate General of DIKTI-Kemendiknas through the Hasanuddin University BPPDN in 2019/2020 and the PDD Grant at Hasanuddin University in 2020/2021.

Author's Declaration

Authors' contributions and responsibilities

The authors made substantial contributions to the conception and design of the study. The authors took responsibility for data analysis, interpretation and discussion of results. The authors read and approved the final manuscript.

Funding

This research was funded by the Ministry of Research, Technology and Higher Education of the Republic of Indonesia through Doctoral Dissertation Research (PDD) in 2021 which was managed by the Hasanuddin University Research and Community Service Institute (Research Grant Number: 7/E1/KP. PTNBH/2021).

Availability of data and materials

All data are available from the authors.

Competing interests

The authors declare no competing interest.

Additional information

No additional information from the authors.

References

[1] S. Ramalingam, E. Murugesan, P. Ganesan, and S. Rajendiran, "Characteristics analysis of julifora biodiesel derived from different production methods," *Fuel*, vol. 280, p. 118579, 2020, doi: 10.1016/j.fuel.2020.118579.

[2] S. Chen, Q. Zhang, P. Andrews-Speed, and B. Mclellan, "Quantitative assessment of the environmental risks of geothermal energy: A review," *Journal of environmental management*, vol. 276, p. 111287, 2020, doi:

10.1016/j.jenvman.2020.111287.

[3] B. Xu, J. Xu, and Z. Chen, “Heat transfer study in solar collector with energy storage,” *International Journal of Heat and Mass Transfer*, vol. 156, p. 119778, 2020, doi: 10.1016/j.ijheatmasstransfer.2020.119778.

[4] B. Stürmer, D. Leiers, V. Anspach, E. Brügging, D. Scharfy, and T. Wissel, “Agricultural biogas production: A regional comparison of technical parameters,” *Renewable Energy*, vol. 164, pp. 171–182, 2021, doi: 10.1016/j.renene.2020.09.074.

[5] C. Valderrama, V. Quintero, and V. Kafarov, “Energy and water optimization of an integrated bioethanol production process from molasses and sugarcane bagasse: A Colombian case,” *Fuel*, vol. 260, p. 116314, 2020, doi: 10.1016/j.fuel.2019.116314.

[6] M. A. A. Farid, A. M. Roslan, M. A. Hassan, M. Y. Hasan, M. R. Othman, and Y. Shirai, “Net energy and techno-economic assessment of biodiesel production from waste cooking oil using a semi-industrial plant: A Malaysia perspective,” *Sustainable Energy Technologies and Assessments*, vol. 39, p. 100700, 2020, doi: 10.1016/j.seta.2020.100700.

[7] S. M. A. Rahman, I. M. R. Fattah, S. Maitra, and T. M. I. Mahlia, “A ranking scheme for biodiesel underpinned by critical physicochemical properties,” *Energy Conversion and Management*, vol. 229, p. 113742, 2021, doi: 10.1016/j.enconman.2020.113742.

[8] N. A. Fauzan, E. S. Tan, F. L. Pua, and G. Muthaiyah, “Physiochemical properties evaluation of Calophyllum inophyllum biodiesel for gas turbine application,” *South African Journal of Chemical Engineering*, vol. 32, pp. 56–61, 2020, doi: 10.1016/j.sajce.2020.02.001.

[9] N. Rajendran and B. Gurunathan, “Optimization and technoeconomic analysis of biooil extraction from Calophyllum inophyllum L. seeds by ultrasonic assisted solvent oil extraction,” *Industrial Crops and Products*, vol. 162, p. 113273, 2021, doi: 10.1016/j.indcrop.2021.113273.

[10] A. Arumugam and P. Sankaranarayanan, “Biodiesel production and parameter optimization: An approach to utilize residual ash from sugarcane leaf, a novel heterogeneous catalyst, from Calophyllum inophyllum oil,” *Renewable Energy*, vol. 153, pp. 1272–1282, 2020, doi: 10.1016/j.renene.2020.02.101.

[11] R. Wahyuni, C. Handoko, and R. Agustarini, “Preliminary study on the flowering and fruiting behaviors of nyamplung (Calophyllum inophyllum Linn.),” *Indonesian Journal of Forestry Research*, vol. 9, no. 1, pp. 39–48, 2012, doi: 10.20886/ijfr.2012.9.1.39-48.

[12] A. Arumugam and V. Ponnusami, “Biodiesel production from Calophyllum inophyllum oil a potential non-edible feedstock: An overview,” *Renewable Energy*, vol. 131, pp. 459–471, 2019, doi: 10.1016/j.renene.2018.07.059.

[13] H. W. Aparamarta, S. Gunawan, H. Husin, B. Azhar, and H. T. Aditya, “The effect of high oleic and linoleic fatty acid composition for quality and economical of biodiesel from crude Calophyllum inophyllum oil (CCIO) with microwave-assisted extraction (MAE), batchwise solvent extraction (BSE), and combination of MAE–BSE meth,” *Energy Reports*, vol. 6, pp. 3240–3248, 2020, doi: 10.1016/j.egyr.2020.11.197.

[14] T. F. Adepoju, “Synthesis of biodiesel from Annona muricata–Calophyllum inophyllum oil blends using calcined waste wood ash as a heterogeneous base catalyst,” *MethodsX*, vol. 8, p. 101188, 2021, doi: 10.1016/j.mex.2020.101188.

[15] J. Liu, Y. Nan, and L. L. Tavlarides, “Continuous production of ethanol-based biodiesel under subcritical conditions employing trace amount of homogeneous catalysts,” *Fuel*, vol. 193, pp. 187–196, 2017, doi: 10.1016/j.fuel.2016.12.058.

[16] E. G. Al-Sakkari *et al.*, “Esterification of high FFA content waste cooking oil through different techniques including the utilization of cement kiln dust as a heterogeneous catalyst: A comparative study,” *Fuel*, vol. 279, p. 118519, 2020, doi: 10.1016/j.fuel.2020.118519.

[17] S. Pandian, A. S. Saravanan, P. Sivanandi, M. Santra, and V. K. Booramurthy, “Application of heterogeneous acid catalyst derived from biomass for biodiesel process intensification: a comprehensive review,” *Refining Biomass*

Residues for Sustainable Energy and Bioproducts, pp. 87–109, 2020, doi: 10.1016/B978-0-12-818996-2.00004-1.

[18] A. Bušić *et al.*, "Recent trends in biodiesel and biogas production," *Food technology and biotechnology*, vol. 56, no. 2, p. 152, 2018, doi: 10.17113/ftb.56.02.18.5547.

[19] O. Ogunkunle and N. A. Ahmed, "A review of global current scenario of biodiesel adoption and combustion in vehicular diesel engines," *Energy Reports*, vol. 5, pp. 1560–1579, 2019, doi: 10.1016/j.egyr.2019.10.028.

[20] E. Dahdah *et al.*, "Biodiesel production from refined sunflower oil over Ca–Mg–Al catalysts: Effect of the composition and the thermal treatment," *Renewable Energy*, vol. 146, pp. 1242–1248, 2020, doi: 10.1016/j.renene.2019.06.171.

[21] I. Ahmad and R. Dhar, "Sulfonic acid-functionalized solid acid catalyst in esterification and transesterification reactions," *Catalysis Surveys from Asia*, vol. 21, no. 2, pp. 53–69, 2017, doi: 10.1007/s10563-017-9226-1.

[22] V. SathyaSelvabala, D. K. Selvaraj, J. Kalimuthu, P. M. Periyaraman, and S. Subramanian, "Two-step biodiesel production from Calophyllum inophyllum oil: optimization of modified β-zeolite catalyzed pre-treatment," *Bioresource technology*, vol. 102, no. 2, pp. 1066–1072, 2011, doi: 10.1016/j.biortech.2010.08.052.

[23] O. O. Ayodele and F. A. Dawodu, "Production of biodiesel from Calophyllum inophyllum oil using a cellulose-derived catalyst," *biomass and bioenergy*, vol. 70, pp. 239–248, 2014, doi: 10.1016/j.biombioe.2014.08.028.

[24] L. Kolo, F. Firdaus, and P. Taba, "The use of MCM-48-nCaO AS catalyst in esterification reaction of nyamplung seed oil (Calophyllum inophyllum L.)," *Jurnal Akta Kimia Indonesia (Indonesia Chimica Acta)*, vol. 8, no. 20, pp. 1–10, 2015, doi: 10.20956/ica.v8i2.2466.

[25] H. Juwono, T. Triyono, S. Sutarno, E. Triwahyuni, I. Ulfin, and F. Kurniawan, "Production of Biodiesel from Seed Oil of Nyamplung (Calophyllum inophyllum) by Al-MCM-41 and Its Performance in Diesel Engine," *Indonesian Journal of Chemistry*, vol. 17, no. 2, pp. 316–321, 2017, doi: 10.22146/ijc.24180.

[26] T. M. M. Marso, C. S. Kalpage, and M. Y. Udugala-Ganehenege, "Metal modified graphene oxide composite catalyst for the production of biodiesel via pre-esterification of Calophyllum inophyllum oil," *Fuel*, vol. 199, pp. 47–64, 2017, doi: 10.1016/j.fuel.2017.01.004.

[27] A. Arumugam and V. Ponnusami, "Optimization of recovery of silica from sugarcane leaf ash and Ca/SBA-15 solid base for transesterification of Calophyllum inophyllum oil," *Journal of Sol-Gel Science and Technology*, vol. 74, no. 1, pp. 132–142, 2015, doi: 10.1007/s10971-014-3586-z.

[28] L. U. O. Nan, C. A. O. Yang, L. I. Jin, G. U. O. Wei, and Z. ZHAO, "Preparation of Ni2P/Zr-MCM-41 catalyst and its performance in the hydrodeoxygenation of Jatropha curcas oil," *Journal of Fuel Chemistry and Technology*, vol. 44, no. 1, pp. 76–83, 2016, doi: 10.1016/S1872-5813(16)30007-X.

[29] W.-K. Chen, H.-H. Tseng, M.-C. Wei, E.-C. Su, and I.-C. Chiu, "Transesterification of canola oil as biodiesel over Na/Zr-SBA-15 catalysts: Effect of zirconium content," *International Journal of hydrogen energy*, vol. 39, no. 34, pp. 19555–19562, 2014, doi: 10.1016/j.ijhydene.2014.08.154.

[30] A. Al-Saadi, B. Mathan, and Y. He, "Biodiesel production via simultaneous transesterification and esterification reactions over SrO–ZnO/Al2O3 as a bifunctional catalyst using high acidic waste cooking oil," *Chemical Engineering Research and Design*, vol. 162, pp. 238–248, 2020, doi: 10.1016/j.cherd.2020.08.018.

[31] G. Joshi *et al.*, "Transesterification of Jatropha and Karanja oils by using waste egg shell derived calcium based mixed metal oxides," *Energy Conversion and Management*, vol. 96, pp. 258–267, 2015, doi: 10.1016/j.enconman.2015.02.061.

[32] M. Kaur, R. Malhotra, and A. Ali, "Tungsten supported Ti/SiO2 nanoflowers as reusable heterogeneous catalyst for biodiesel production," *Renewable Energy*, vol. 116, pp. 109–119, 2018, doi: 10.1016/j.renene.2017.09.065.

[33] A. F. Lee, J. A. Bennett, J. C. Manayil, and K. Wilson, "Heterogeneous catalysis for

sustainable biodiesel production via esterification and transesterification," *Chemical Society Reviews*, vol. 43, no. 22, pp. 7887–7916, 2014, doi: 10.1039/C4CS00189C.

[34] J. Wang, G. Wang, Z. Zhang, G. Ouyang, and Z. Hao, "Effects of mesoporous silica particle size and pore structure on the performance of polymer-mesoporous silica mixed matrix membranes," *RSC Advances*, vol. 11, no. 58, pp. 36577–36586, 2021, doi: 10.1039/d1ra05125c.

[35] P. Taba, H. Natsir, S. Fauziah, and M. Ismail, "Adsorpsi Ion Cd(II) oleh Kitosan-Silika Mesopori MCM-48," Universitas Hasanudin, 2012.

[36] M. Pirouzmand, M. M. Anakhatoon, and Z. Ghasemi, "One-step biodiesel production from waste cooking oils over metal incorporated MCM-41; positive effect of template," *Fuel*, vol. 216, pp. 296–300, 2018, doi: 10.1016/j.fuel.2017.11.138.

[37] F. Rajabi and R. Luque, "An efficient renewable-derived surfactant for aqueous esterification reactions," *RSC Advances*, vol. 4, no. 10, pp. 5152–5155, 2014, doi: 10.1039/c3ra45757e.

[38] F. Rajabi and R. Luque, "Highly ordered mesoporous functionalized pyridinium protic ionic liquids framework as efficient system in esterification reactions for biofuels production," *Molecular Catalysis*, vol. 498, p. 111238, 2020, doi: 10.1016/j.mcat.2020.111238.

[39] A. B. Fadhil, A. M. Aziz, and M. H. Al-Tamer, "Biodiesel production from Silybum marianum L. seed oil with high FFA content using sulfonated carbon catalyst for esterification and base catalyst for transesterification," *Energy Conversion and Management*, vol. 108, pp. 255–265, 2016, doi: 10.1016/j.enconman.2015.11.013.

[40] D. O. Onukwuli, L. N. Emembolu, C. N. Ude, S. O. Aliozo, and M. C. Menkiti, "Optimization of biodiesel production from refined cotton seed oil and its characterization," *Egyptian Journal of Petroleum*, vol. 26, no. 1, pp. 103–110, 2017, doi: 10.1016/j.ejpe.2016.02.001.

[41] M. C. G. Souza, M. F. de Oliveira, A. T. Vieira, A. M. de Faria, and A. C. F. Batista, "Methylic and ethylic biodiesel production from crambe oil (Crambe abyssinica): New aspects for yield and oxidative stability," *Renewable Energy*, vol. 163, pp. 368–374, 2021, doi: 10.1016/j.renene.2020.08.073.

[42] M. Y. Chang, E.-S. Chan, and C. P. Song, "Biodiesel production catalysed by low-cost liquid enzyme Eversa® Transform 2.0: Effect of free fatty acid content on lipase methanol tolerance and kinetic model," *Fuel*, vol. 283, p. 119266, 2021, doi: 10.1016/j.fuel.2020.119266.

[43] P. Taba, P. Budi, A. A. Gau, Y. Hala, I. W. Sutapa, and J. Manga, "Mesoporous silica modified with amino group (NH2-MCM-48) as adsorbent of Ag (I) and Cr (III) in water," *Rasayan J. Chem*, vol. 14, no. 1, pp. 204–211, 2021, doi: 10.31788/RJC.2021.1415963.

[44] Y.-T. Wang, Z. Fang, and F. Zhang, "Esterification of oleic acid to biodiesel catalyzed by a highly acidic carbonaceous catalyst," *Catalysis Today*, vol. 319, pp. 172–181, 2019, doi: 10.1016/j.cattod.2018.06.041.

[45] Y. Xia and R. Mokaya, "A study of the behaviour of mesoporous silicas in OH/CTABr/H 2 O systems: phase dependent stabilisation, dissolution or semi-pseudomorphic transformation," *Journal of Materials Chemistry*, vol. 13, no. 12, pp. 3112–3121, 2003, doi: 10.1039/b305404g.

[46] A. K. Basumatary, R. Vinoth Kumar, K. Pakshirajan, and G. Pugazhenthi, "Removal of trivalent metal ions from aqueous solution via cross-flow ultrafiltration system using zeolite membranes," *Journal of Water Reuse and Desalination*, vol. 7, no. 1, pp. 66–76, 2017, doi: 10.2166/wrd.2016.211.

[47] T. Vrålstad, G. Øye, M. Stöcker, and J. Sjöblom, "Synthesis of comparable Co-MCM-48 and Co-MCM-41 materials containing high cobalt contents," *Microporous and mesoporous materials*, vol. 104, no. 1–3, pp. 10–17, 2007, doi: 10.1016/j.micromeso.2006.06.006.

[48] Y. Ding, C. Zhao, Y. Li, Z. Ma, and X. Lv, "Effect of calcination temperature on the structure and catalytic performance of the cu-mcm-41 catalysts for the synthesis of dimethyl carbonate," *Química Nova*, vol. 41, no. 10, pp. 1156–1161, 2018, doi: 10.21577/0100-4042.20170291.

[49] N. T. Nguyen and V. A. Nguyen, "Synthesis, Characterization, and Photocatalytic Activity

of ZnO Nanomaterials Prepared by a Green, Nonchemical Route," *Journal of Nanomaterials*, vol. 2020, pp. 1–8, 2020, doi: 10.1155/2020/1768371.

[50] X. Li, W. Chen, Y. Tang, and L. Li, "Relationship between the structure of Fe-MCM-48 and its activity in catalytic ozonation for diclofenac mineralization," *Chemosphere*, vol. 206, pp. 615–621, 2018, doi: 10.1016/j.chemosphere.2018.05.066.

[51] J. C. K. Lam *et al.*, "Vibrational spectroscopy of low-k/ultra-low-k dielectric materials on patterned wafers," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, vol. 29, no. 5, p. 51513, 2011, doi: 10.1116/1.3625099.

[52] A. Patel and D. Pithadia, "Low temperature synthesis of bio-fuel additives via valorisation of glycerol with benzaldehyde as well as furfural over a novel sustainable catalyst, 12-tungstosilicic acid anchored to ordered cubic nano-porous MCM-48," *Applied Catalysis A: General*, vol. 602, p. 117729, 2020, doi: 10.1016/j.apcata.2020.117729.

[53] D. Jamshidi and M. R. Sazegar, "Antibacterial activity of a novel biocomposite chitosan/graphite based on zinc-grafted mesoporous silica nanoparticles," *International Journal of Nanomedicine*, vol. 15, p. 871, 2020, doi: 10.2147/IJN.S234043.

[54] M. R. Sazegar, A. Dadvand, and A. Mahmoudi, "Novel protonated Fe-containing mesoporous silica nanoparticle catalyst: excellent performance cyclohexane oxidation," *RSC advances*, vol. 7, no. 44, pp. 27506–27514, 2017, doi: 10.1039/c7ra02280h.

[55] P. Taba, P. Budi, and A. Y. Puspitasari, "Adsorption of heavy metals on amine-functionalized MCM-48," in *IOP conference series: materials science and engineering*, 2017, vol. 188, no. 1, p. 12015, doi: 10.1088/1757-899x/188/1/012015.

[56] D. Guliani, A. Sobti, and A. P. Toor, "Comparative study on Graphene Oxide and MCM-48 based catalysts for esterification reaction," *Materials Today: Proceedings*, vol. 41, pp. 805–811, 2021, doi: 10.1016/j.matpr.2020.08.751.

[57] P. Taba, R. D. P. Mustafa, L. M. Ramang, and A. H. Kasim, "Adsorption of Pb2+ on Thiol-functionalized Mesoporous Silica, SH-MCM-48," in *Journal of Physics: Conference Series*, 2018, vol. 979, no. 1, p. 12058, doi: 10.1088/1742-6596/979/1/012058.

[58] H. Aghaei *et al.*, "Investigation on bioactivity and cytotoxicity of mesoporous nano-composite MCM-48/hydroxyapatite for ibuprofen drug delivery," *Ceramics International*, vol. 40, no. 5, pp. 7355–7362, 2014, doi: 10.1016/j.ceramint.2013.12.079.

[59] R. Taheri, N. Bahramifar, M. R. Zarghami, H. Javadian, and Z. Mehraban, "Nanospace engineering and functionalization of MCM-48 mesoporous silica with dendrimer amines based on [1, 3, 5]-triazines for selective and pH-independent sorption of silver ions from aqueous solution and electroplating industry wastewater," *Powder Technology*, vol. 321, pp. 44–54, 2017, doi: 10.1016/j.powtec.2017.08.022.

[60] M. Zdujić *et al.*, "Synthesis of CaOSiO2 compounds and their testing as heterogeneous catalysts for transesterification of sunflower oil," *Advanced Powder Technology*, vol. 30, no. 6, pp. 1141–1150, 2019, doi: 10.1016/j.apt.2019.03.009.

[61] I. Klapiszewska, A. Parus, Ł. Ławniczak, T. Jesionowski, Ł. Klapiszewski, and A. Ślosarczyk, "Production of antibacterial cement composites containing ZnO/lignin and ZnO–SiO2/lignin hybrid admixtures," *Cement and Concrete Composites*, vol. 124, p. 104250, 2021, doi: 10.1016/j.cemconcomp.2021.104250.

[62] H. Helmiyati and R. P. Suci, "Nanocomposite of cellulose-ZnO/SiO2 as catalyst biodiesel methyl ester from virgin coconut oil," in *AIP Conference Proceedings*, 2019, vol. 2168, no. 1, p. 20063, doi: 10.1063/1.5132490.

[63] N. A. Al-Tayyar, A. M. Youssef, and R. R. Al-Hindi, "Antimicrobial packaging efficiency of ZnO-SiO2 nanocomposites infused into PVA/CS film for enhancing the shelf life of food products," *Food Packaging and Shelf Life*, vol. 25, p. 100523, 2020, doi: 10.1016/j.fpsl.2020.100523.

[64] Z. Chu, C. A. Dreiss, and Y. Feng, "Smart wormlike micelles," *Chemical Society Reviews*, vol. 42, no. 17, pp. 7174–7203, 2013, doi: 10.1039/c3cs35490c.

[65] T. Kimura, K. Kuroda, Y. Sugahara, and K. Kuroda, "Esterification of the silanol groups in the mesoporous silica derived from kanemite," *Journal of Porous Materials*, vol. 5, no. 2, pp. 127–132, 1998, doi: 10.1023/A:1009641304742.

[66] Z. Talha *et al.*, "Al-Rich ordered mesoporous silica SBA-15 materials: synthesis, surface characterization and acid properties," *Catalysis Letters*, vol. 147, no. 8, pp. 2116–2126, 2017, doi: 10.1007/s10562-017-2103-8.

[67] A. F. Alhikami, C.-E. Yao, and W.-C. Wang, "A study of the spray ignition characteristics of hydro-processed renewable diesel, petroleum diesel, and biodiesel using a constant volume combustion chamber," *Combustion and Flame*, vol. 223, pp. 55–64, 2021, doi: 10.1016/j.combustflame.2020.09.033.

[68] J. Zhang, Y. Guo, D. Pau, K. Li, K. Xie, and Y. Zou, "Pyrolysis kinetics and determination of organic components and N-alkanes yields of Karamay transformer oil using TG, FTIR and Py-GC/MS analyses," *Fuel*, vol. 306, p. 121691, 2021, doi: 10.1016/j.fuel.2021.121691.