

CLAY-BASED PILLARED CATALYSTS FOR SUSTAINABLE METHYL OLEATE PRODUCTION

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ABSTRACT

This research focuses on the catalytic dehydration of methyl 12-hydroxystearate, a derivative of non-edible castor oil, into methyl oleate using vanadia-pillared montmorillonite catalysts modified with zirconium, iron, and cerium. Structural and physicochemical analyses were conducted to establish correlations between catalyst properties and performance. The unmodified vanadia-pillared clay demonstrated exceptional activity, achieving nearly complete conversion (99.94%) with high selectivity (84.48%) toward methyl oleate. Among the modified systems, cerium doping significantly improved yield and selectivity, whereas iron incorporation reduced efficiency due to enhanced formation of the trans-isomer. The catalytic outcomes were strongly influenced by the balance of weak and medium acid sites, highlighting the importance of acid site engineering in catalyst design. The broader implications of this work lie in advancing sustainable oleochemical production. By enabling direct dehydration of renewable feedstocks, these catalysts reduce the need for additional derivatisation steps, lower energy requirements, and improve product selectivity.

Keywords: Keywords: Vanadia-Pillared Clay, Zirconium, Iron, Cerium, Castor Oil, Dehydration Reactions

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INTRODUCTION

Methyl oleate (MO) is a versatile compound with wide applications in detergents, emulsifiers, stabilisers, textile finishing, cosmetics, biodiesel, and polymer synthesis.^{1,2} Its biodegradability and low toxicity have further expanded interest, with recent studies reporting activity against multidrug-resistant ESBL pathogens.³ In 2023, the Asia-Pacific region led global MO consumption, with a projected 4.37% CAGR from 2024 to 2030, though rising feedstock and processing costs remain barriers to growth.⁴ Conventionally, MO is synthesised via esterification of oleic-acid-rich vegetable oils such as soybean, sunflower, and canola.⁵⁻⁷ While edible oils are avoided due to cost, castor oil, a non-edible renewable resource, provides methyl 12-hydroxystearate (M12HSA), a promising precursor. Hydrogenation of castor-oil methyl esters yields ~87% MO, positioning M12HSA as a strategic substrate for targeted synthesis.⁸ Montmorillonite smectite clay (MMT) offers a layered framework that can be pillared with metal oxides, enhancing surface area, porosity, acidity, and stability.^{9,10} Vanadia-pillared clays (V-PILC), despite notable redox and Lewis acidity, remain underexplored, representing only 0.01% of reported pillared-clay studies.^{11,12} Incorporation of zirconium, iron, or cerium diversifies acidity and redox properties.¹³⁻¹⁵ However, no prior work has examined dehydration isomerisation of M12HSA to MO using V-PILC or its doped analogues. This study addresses that gap by synthesising and characterising V-PILC catalysts and evaluating their efficiency in selectively converting castor-oil derivatives into MO. The work contributes to SDG-9.5 by advancing scientific innovation and sustainable industrial technologies.

EXPERIMENTAL

Material and Methods

Montmorillonite K powder (MMT) from Sigma-Aldrich has a chemical composition of oxygen (62.85%), silicon (27.66%), aluminium (5.81%), potassium (0.63%), and magnesium (0.80%). Ammonium metavanadate (AR) from Sisco Research Laboratories Pvt. Ltd., oxalic acid (AR), and zirconium oxychloride octahydrate (AR) from Loba Chemie Pvt. Ltd. Ferric chloride hexahydrate (AR) grade and

Catalysts Synthesis

Catalysts Characterization

Catalytic Activity Study

Chemical reaction scheme showing the conversion of Methyl 12-hydroxystearate to Methyl oleate. The reaction is catalyzed by V-PILC / modified V-PILCs and involves the loss of water ($\text{-H}_2\text{O}$).

Reactant: Methyl 12-hydroxystearate

Product: Methyl oleate

Fig.-1: Schematic Representation of Dehydration of M12HSA

RESULTS AND DISCUSSION

XRD Analysis and Surface Area–Pore Volume Measurements

BET analysis revealed that pillaring increased the surface area and enlarged pore volume. Introducing Zr, Fe, and Ce progressively reduced these values most in V-PILC-Ce and least in V-PILC-Zr (Table-1), consistent with pore blockage by uniformly distributed metal species.

Thermogravimetric Analysis

TGA (30–790 °C, air) Fig.-3, showed ~7–8 % weight loss below 100 °C from physisorbed water and a further mass loss between 150–580 °C attributed to chemisorbed water release¹⁷ or pillar dehydroxylation. Above 600 °C, minor clay-layer degradation was observed. All Zr-, Fe-, and Ce-doped V-PILCs followed

this pattern but exhibited lower weight loss at high temperature than undoped V-PILC, with thermal stability above 600 °C increasing alongside dopant loading.

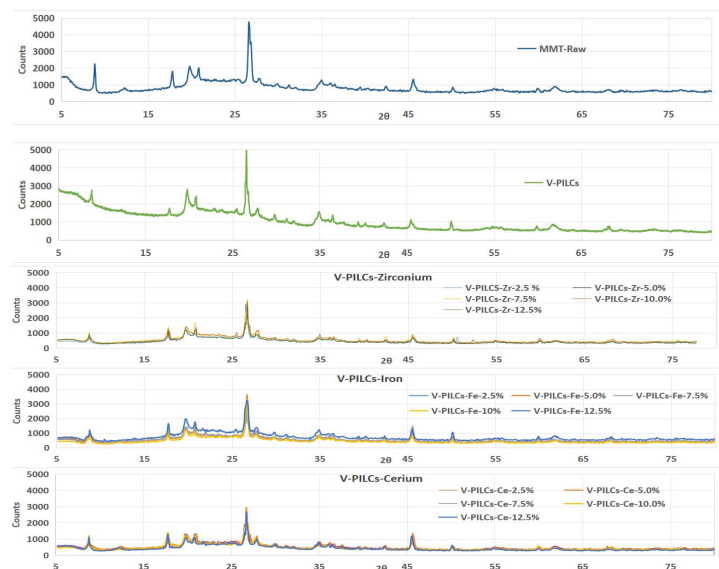


Fig.-2: XRD Graphs of Montmorillonite K-10, V-PILCs, V-PILCs Modified with Zirconium, Iron and Cerium Metal Loading (2.5-12.5 wt.%) from Top to Bottom

Table-1: BET Surface Area, Pore Volume and XRD d001 of V-PILC and V-PILC-, Iron, Zirconium and Cerium Catalysts with Metal Concentration of 2.5, 5.0, 7.5, 10.0 and 12.5% Each

Catalysts	BET Surface area (m ² /g)	Pore volume (cm ³ /g)	XRD 'd001' value(Å)
Montmorillonite clay	251.9	0.44	9.99
V-PILCs	266.1	0.44	12.52
V-PILS's-Zirconium 2.5%	206.2	0.39	12.77
V-PILS's- Zirconium 5.0%	197.0	0.38	12.92
V-PILS's- Zirconium 7.5%	190.5	0.38	12.92
V-PILS's- Zirconium 10.0 %	182.5	0.31	12.89
V-PILS's- Zirconium 12.5%	179.2	0.25	12.92
V-PILS's-Iron 2.5%	192.1	0.38	12.49
V-PILS's- Iron 5.0%	178.7	0.35	12.63
V-PILS's- Iron 7.5%	169.4	0.34	12.35
V-PILS's- Iron 10.0 %	167.8	0.25	12.63
V-PILS's- Iron 12.5%	165.4	0.22	12.21
V-PILS's-Cerium 2.5%	170.7	0.35	12.92
V-PILS's-Cerium 5.0%	158.5	0.30	12.92
V-PILS's-Cerium 7.5%	149.1	0.28	12.35
V-PILS's-Cerium 10.0 %	145.9	0.21	12.49
V-PILS's-Cerium 12.5 %	142.6	0.23	12.63

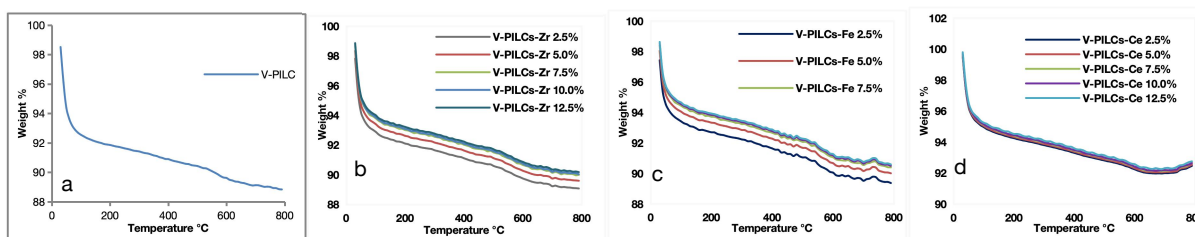


Fig.-3: TGA Graph: a. V-PILC, b. V-PILC-Zr, c. V-PILC-Fe, and d. V-PILC-Ce with Metal Concentration of 2.5, 5.0, 7.5, 10.0 and 12.5% each vs. Temperature

Fourier Transform Infrared Spectroscopy (ATR-FTIR) Analysis

FTIR/ATR spectra (Fig.-4) for raw montmorillonite, V-PILC, and modified V-PILC doped with zirconium, iron, and cerium at different metal concentrations show no significant difference in functional groups. FTIR-ATR spectra of V-PILC and its Zr, Fe, and Ce-doped variants display a faint 3427cm^{-1} -OH band only in the doped samples, indicating limited adsorbed water. All materials preserve the montmorillonite fingerprint: Si-O at 1041cm^{-1} , Al-OH-Al at 921cm^{-1} , quartz-related Si-O/Si-O-Al at 790 and 690cm^{-1} , and Si-O-Al stretches near 540 and 470cm^{-1} in all doped catalysts, suggesting that the natural montmorillonite clay structure remains largely intact after pillaring and doping treatments.¹⁸ The lack of distinct Zr, Fe, or Ce bands confirms their low concentration and uniform dispersion within the interlayers.

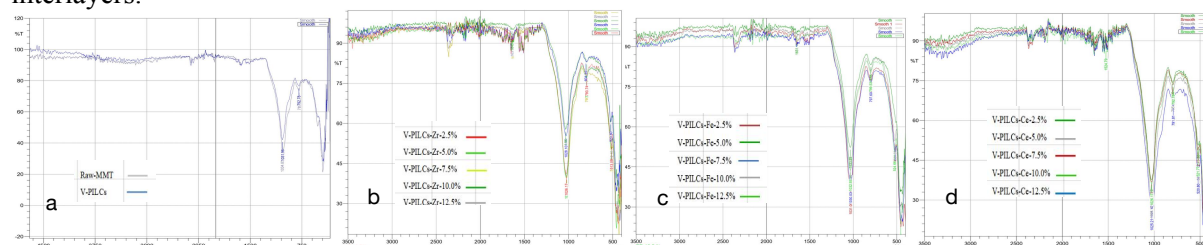


Fig.-4: FTIR Graph for a. Raw Montmorillonite and V-PILC, b. V-PILC-Zr, c. V-PILC-Fe and d. V-PILC-Ce with Metal Concentrations of 2.5, 5.0, 7.5, 10.0 and 12.5% each. Plot of Transmittance vs cm^{-1}

Elemental Analysis

Scanning electron microscopy (SEM) analysis with EDS mapping showed that V-PILC is composed of 68.02% oxygen, 5.52% aluminium, 23.66% silica, and 2.81% vanadium. Catalysts doped with zirconium (5.0%), iron (5.0%), and cerium (5.0%) showed a metal concentrations of 4.13%, 4.47%, and 1.44%, respectively, with an even distribution of metal throughout the clay (Fig.-5).

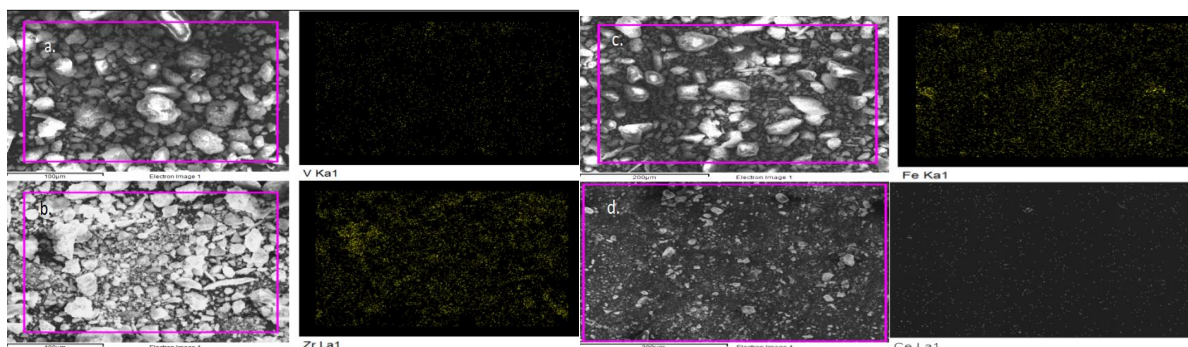


Fig.-5: SEM Graphs for Surface Morphology and EDS Mapping of a. V-PILCs, b. V-PILCs-Zr (5.0%), c. V-PILCs-Fe (5.0%) and V-PILCs-Ce (5.0%) from Top to Bottom

Acidity Measurements

NH_3 -TPD analysis shows introducing Fe, Zr, or Ce at low loadings slightly boosts strong-acid sites, but higher dopant levels progressively reduce total, medium, and strong acidity (Table-2). This reflects partial coverage of Brønsted protons by less acidic metal cations in the clay interlayers, weakening electrostatic interactions and shifting the balance toward weaker acid centers.²⁰

Table-2: Acidity Measurement using Ammonia TPD V-PILC, V-PILC-Zr, V-PILC-Fe and V-PILC-Ce Classification Based on Ammonia Desorption Temperature

Catalysts	Low ($< 200\text{ }^\circ\text{C}$) $\mu\text{mol/g}$	Moderate ($201\text{--}400\text{ }^\circ\text{C}$) $\mu\text{mol/g}$	Strong ($> 500\text{ }^\circ\text{C}$) $\mu\text{mol/g}$	Total acidity $\mu\text{mol/g}$
V-PILCs	132.00	413.00	812.00	1357
V-PILS's-Zr-2.5%	132.96	244.01	1752.03	2129
V-PILS's-Zr-5.0%	136.24	249.35	1435.4	1821
V-PILS's-Zr-7.5%	154.63	263.92	714.45	1133

V-PILS's-Zr-10.0 %	181.72	156.78	587.50	926
V-PILS's-Zr-12.5%	191.86	85.66	378.49	656
V-PILS's-Fe-2.5%	130.42	123.16	1171.42	1425
V-PILS's-Fe-5.0%	133.85	127.28	1097.87	1359
V-PILS's-Fe-7.5%	133.99	136.43	813.58	1084
V-PILS's-Fe-10.0 %	127.39	149.97	629.64	907
V-PILS's-Fe-12.5%	134.63	150.41	373.96	659
V-PILS's-Ce-2.5%	193.79	261.06	1520.15	1975
V-PILS's-Ce-5.0%	219.21	212.56	1099.23	1531
V-PILS's-Ce-7.5%	220.93	223.09	620.98	1065
V-PILS's-Ce-10.0 %	235.48	229.48	361.04	826
V-PILS's-Ce-12.5%	239.09	230.17	245.74	715

Product Characterization Results

Table-3 summarizes the product distribution obtained during the dehydration of methyl 12-hydroxystearate (M12HSA) using V-PILC and its Fe-, Zr-, and Ce-doped variants at different metal loadings. The data highlight that undoped V-PILC achieved the highest selectivity toward methyl oleate (cis-isomer), while Fe-doped catalysts showed reduced efficiency due to increased formation of the trans-isomer methyl elaidate. In contrast, Zr- and Ce-modified systems maintained relatively high conversion and selectivity, with Ce-doping particularly enhancing methyl oleate yield at moderate loadings. This comparison underscores the critical role of dopant type and concentration in influencing catalytic performance and product selectivity.

Table-3: Dehydration of M12HSA: Catalysts- V-PILC and V-PILC-Fe, Zr, Ce (2.5, 5.0, 7.5, 10.0 and 12.5%), Catalyst concentration – 1%, Temperature- 195-200 °C, Reaction Time -1 h

Catalysts	M12HSA %	Methyl Palmitate %	Methyl Stearate %	Other fatty acids %	Methyl Elaidate % (trans-isomer)	Methyl Oleate % (cis-isomer)
M-12HSA starting	88.06	1.05	9.43	1.04	-	0.42
V-PILCs	0.06	1.02	9.55	2.69	2.25	84.43
V-PILC-Zr-2.5%	3.65	1.34	11.70	2.63	2.10	78.58
V-PILC-Zr-5.0%	2.16	1.07	10.62	1.27	1.90	82.98
V-PILC-Zr-7.5%	6.03	1.10	10.06	3.42	2.44	76.96
V-PILC-Zr-10.0 %	8.29	0.97	11.58	3.15	2.98	73.03
V-PILC-Zr-12.5%	9.85	1.72	12.34	1.60	2.91	71.58
V-PILC-Fe-2.5%	4.06	1.09	12.72	2.13	10.07	69.93
V-PILC-Fe-5.0%	1.75	1.03	9.67	3.30	10.16	74.09
V-PILC-Fe-7.5%	5.74	1.10	9.06	3.47	11.74	68.89
V-PILC-Fe-10.0 %	8.85	1.08	9.28	3.71	12.47	64.61
V-PILC-Fe-12.5%	9.59	1.07	9.94	3.12	13.25	63.03
V-PILC-Ce-2.5%	5.95	1.10	11.59	1.11	0.45	79.80
V-PILC-Ce-5.0%	0.47	1.00	11.23	1.05	0.13	86.12
V-PILC-Ce-7.5%	0.64	0.99	12.13	1.60	0.96	83.68
V-PILC-Ce-10.0 %	3.41	0.82	11.66	1.88	1.09	81.14
V-PILC-Ce-12.5%	4.20	1.10	12.98	2.66	0.98	78.08

Table-4 presents a comparative evaluation of catalytic performance for V-PILC and its Fe-, Zr-, and Ce-doped variants at different loadings. The results clearly show that undoped V-PILC achieved the highest conversion of M12HSA (99.9%) with 84.5% selectivity toward methyl oleate. Among the doped systems, Ce-modified catalysts exhibited superior efficiency, with the 5% Ce loading delivering the best yield and selectivity. Zr-doped catalysts maintained moderate performance, with optimal selectivity observed at 5% loading, while Fe-doped catalysts consistently showed lower selectivity due to enhanced trans-isomer formation. The correlation between weak and medium acidity values and catalytic activity highlights the importance of balanced acid site distribution in achieving high conversion and selectivity.

Table-4: Comparison of Conversion of M12HSA, Selectivity of MO, Yield of MO, Sum of Weak and Medium Acidity, of Product from V-PILC and Zr, Fe and Ce Doped V-PILC Catalysed Reaction with Different Concentration

Catalysts	Conversion of M12HSA (%)	Selectivity for Methyl oleate (%)	Yield of Methyl oleate (%)	Weak + Medium acidity $\mu\text{mol/g}$
V-PILC	99.9	84.5	84.4	545.00
V-PILC-Zr-2.5%	95.9	81.6	78.2	376.97
V-PILC-Zr-5.0%	97.6	84.8	82.7	385.59
V-PILC-Zr-7.5%	93.2	81.9	76.3	418.55
V-PILC-Zr-10.0 %	90.6	79.6	72.1	338.50
V-PILC-Zr-12.5%	88.8	79.4	70.5	277.52
V-PILC-Fe-2.5%	95.4	72.9	69.5	253.58
V-PILC-Fe-5.0%	98.0	75.4	73.9	261.13
V-PILC-Fe-7.5%	93.5	73.1	68.3	270.42
V-PILC-Fe-10.0 %	90.0	70.9	63.8	277.36
V-PILC-Fe-12.5%	89.1	69.7	62.1	285.04
V-PILC-Ce-2.5%	93.2	84.9	79.1	454.85
V-PILC-Ce-5.0%	99.5	86.5	86.1	431.77
V-PILC-Ce-7.5%	99.3	84.2	83.6	444.02
V-PILC-Ce-10.0 %	96.1	84.0	80.8	464.96
V-PILC-Ce-12.5%	95.2	81.5	77.6	469.26

The comparative evaluation of vanadia-pillared montmorillonite and its doped variants demonstrates that catalytic efficiency is strongly governed by the interplay between surface area, pore accessibility, and acid site distribution. Undoped V-PILC, with abundant weak and medium acid sites, achieved the highest conversion and selectivity toward methyl oleate, confirming the intrinsic suitability of vanadia pillaring for dehydration reactions. Cerium modification further optimised acidity and pore characteristics, delivering superior yield and selectivity at moderate loadings, while zirconium maintained moderate performance and iron consistently promoted trans-isomer formation, reducing efficiency. These results provide new insights into how dopant type and concentration influence structure–activity relationships in pillared clays. Beyond advancing fundamental understanding, this study contributes to the broader oleochemical and biodiesel research landscape by demonstrating a sustainable pathway for converting non-edible castor-oil derivatives into high-value methyl oleate. The findings highlight the potential of tailored pillared clays as scalable, environmentally friendly catalysts that minimise derivatisation steps and energy demand. Academically, the work fills a critical research gap by introducing V-PILC systems into dehydration–isomerisation chemistry, while practically, it supports industrial innovation in renewable feedstock utilisation. In alignment with SDG 9.5, the study strengthens the link between scientific research and sustainable industrial technologies, paving the way for future catalyst design strategies in green chemistry.

CONCLUSION

The physico-chemical analyses confirmed the successful synthesis of vanadia-pillared montmorillonite (V-PILC) catalysts via wet impregnation, with zirconium, iron, and cerium modifications effectively incorporated into the clay framework. Catalytic evaluation demonstrated that undoped V-PILC achieved the highest conversion and selectivity toward methyl oleate, while cerium doping further enhanced yield and selectivity at moderate loadings. Zirconium maintained moderate efficiency, whereas iron consistently promoted trans-isomer formation, reducing overall performance. These results highlight the critical role of dopant type and concentration in tailoring acidity and pore accessibility to optimise catalytic behaviour. The developed process for converting methyl 12-hydroxystearate from non-edible castor oil into methyl oleate is efficient, environmentally benign, and highly selective, offering a sustainable alternative to conventional edible-oil-based routes. The catalysts are safer to handle and minimise environmental impact, making them suitable for industrial application. Future research should prioritise optimising clay-based pillared systems to enhance selectivity, investigate alternative dopants for

improved acidity and redox control, and undertake scale-up studies to validate industrial applicability. This work contributes directly to SDG-9: Industry, Innovation, and Infrastructure by advancing eco-friendly catalytic technologies, strengthening scientific research, and promoting sustainable industrial development through renewable feedstock utilisation.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-9: Industry, Innovation, and Infrastructure*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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