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Research Article

Vegetal Oil Transesterification Using Tetranuclear Zinc-Diterpene Clusters as the Catalysts

Mayra A. Martínez-Torres[1], Armando Talavera-Alemán[1], Karina Zamudio-Jaime[1], Ana K. Villagómez-Guzmán[1], Lirenny Quevedo-Tinoco[1], José L. Rico[2], Gerardo Rosas[3], Rosa E. del Río[1], Mario A. Gómez-Hurtado[1]*, Gabriela Rodríguez-García[1]*

[1]Instituto de Investigaciones Químico Biológicas, Edificio B-1, Universidad Michoacana de San Nicolás de Hidalgo, Ciudad Universitaria, Morelia, Michoacán 58030, Mexico.
[2]Laboratorio de Catálisis, División de Estudios de Posgrado de la Facultad de Ingeniería Química, Edificio V-1, Universidad Michoacana de San Nicolás de Hidalgo, Ciudad Universitaria, Morelia, Michoacán 58030, Mexico.
[3]Instituto de Investigación en Metalurgia y Materiales, Universidad Michoacana de San Nicolás de Hidalgo, Ciudad Universitaria, Morelia, Michoacán 58030, Mexico.

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Abstract

Organic natural products, particularly vegetal secondary metabolites, represent a highlighted source for molecules usable for many purposes, including synthesizing catalysts. Biocompatible metals can yield interesting coordination complexes to provide sustainable and valuable compounds. In the present paper, the unique in their class (μ4-oxo)-hexakis(μ2-beyerenate)-tetra-zinc(II) (**1**) and (μ4-oxo)-hexakis(μ2-kaurenate)-tetra-zinc(II) (**2**) are suggested as eco-friendly catalysts for transesterification reactions. The heterogeneous/homogeneous catalytic potential of 1 and 2 was revealed using olive oil as an equilibrated saturated-unsaturated fatty acid mixture and methanol as the nucleophile and solvent. Systematic variations in reaction conditions were achieved herein, including temperature, catalyst mass, methanol volume, and reaction time, allowing a yield of up to 97% in the transesterification process. The FAME product was characterized using ^{1}H NMR and GC-MS, and the calorific value of 33.72 MJ/kg was concordant with the literature. The thermogravimetric, powder X-ray diffraction, and Scanning Electron Microscopy experiments complemented the catalyst properties before and after the catalytic tests. This finding suggests that coordination complexes using natural products as ligands represent a new class of potential ecological catalysts from industry and scientific research in crucial chemical reactions.

Keywords: Zinc cluster; Fatty acids; FAME; Catalysis; Vegetal Oil Transesterification; Zinc-Diterpene

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1. Introduction

Ecofriendly sources and procedures are currently required to fulfill actual and future human needs, and biomass is a key strategic source to gain those purposes, including raw materials and final product acquisition. Among those, biofuel highlights since recent statistical estimations suggested that emissions could be reduced by 34% compared to fossil fuels [1]. Furthermore, the ecological impacts of non-renewable fuels should be considered [2] at local and global levels [3]. Therefore, domestic approaches to mitigate such problems for further

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* Corresponding Author.
Email: mario.gomez@umich.mx (M.A. Gómez-Hurtado)
gabriela.rodriguez@umich.mx (G. Rodríguez-García)

global applications are considered essential nowadays [4]. For these purposes, the literature suggests several strategies for biofuel production, including those by esterification [5] or transesterification procedures [6-10], where natural oil and alcohol are used as raw materials, and a homogeneous, heterogeneous, or enzymatic catalyst is essential to promote the chemical reaction. Whatever the case, activating the carbonyl group from fatty acid is required for the subsequent nucleophilic attack by OH from involved alcohol for subsequent ester formation [11]. The thermodynamics of these reactions can be favored by conventional heating or microwave-assisted heating [12-14]. At the end of the reaction process, fatty acid methyl ester (FAME) and glycerol are gained as reaction products [15], where FAME could be used as biofuel and glycerol could be used in the chemical, textile, pharmaceutical, and food industries [16,17]. The advantages and disadvantages of each class of catalyst, which are related to yields, reaction conditions, management, costs, and catalytic capability, have been widely described [15].

Terpenes are the most common among the compound plants synthesize to enhance their survival [18,19]. Such molecules are commonly functionalized with oxygenated moieties [20,21], which our research group has taken advantage of to synthesize coordination complexes using biocompatible metallic centers, thus leading to novel and potential catalysts with sustainable applications.

In a previous research work, the synthesis of oxozinc-diterpene clusters such as (μ_4-oxo)-hexakis(μ_2-beyerenate)-tetra-zinc(II) (**1**) and (μ_4-oxo)-hexakis(μ_2-kaurenate)-tetra-zinc(II) (**2**) using natural kaurenoic or beyerenoic acids from *Perymenium buphthalmoides* was described [22]. It is good to resemble that oxozinc cluster compound types have been studied since 1924 [23]. Since then, oxozinc carboxylate clusters have been used as an efficient catalyst [24] in the transesterification of methyl esters [25], acetylation of alcohols [26], deacetylation of acetates [27], and several other processes from small molecules [28]. Furthermore, the central Zn_4O motif has frequently been used as a key component in constructing metal-organic frameworks (MOFs) [29,30]. The Zn_4O-based MOFs found many practical applications as heterogeneous catalysts for various organic transformations (cycloaddition of CO_2 with epoxides, C–C cross-coupling reactions, cyanosilylation, and C–N bond formation [31].

In the present work, the use of **1** and **2** as catalysts in the transesterification of olive oil with methanol is reported. This experimental model revealed the potential of tetranuclear zinc clusters as catalysts for the first time in the transesterification of robust molecules in a complex glyceride mixture. The catalyst potential was boarded by systematic assays, where reaction conditions, including reaction time, temperature, and catalyst amount variations, were boarded. The use of diterpene-biometal complex compounds as catalysts for transesterification reactions has yet to be published. Thus, current results display the catalytic potential of this rare class of compounds.

2. Materials and Methods

2.1. General Experimental Procedures

The melting point (uncorrected) of catalysts **1** and **2** was determined on a Fisher-Johns apparatus. Specific rotations were determined on a PerkinElmer 341 polarimeter. The 1D NMR spectra were measured at 400 MHz for ^1H and 100 MHz for ^{13}C on a Varian Mercury 400 spectrometer in $CDCl_3$ solution using tetramethylsilane as the internal reference. The elemental analysis was achieved on a Thermo Scientific Flash 2000 instrument at a furnace temperature of 950 °C. Thermal stability was measured on a PerkinElmer STA6000 thermogravimetric analyzer (TGA). X-ray powder diffraction (XRD) analysis was achieved on a Bruker D8 Advance Diffractometer, DAVINCI, in an angular range of 10–100 ° (Kα copper radiation). The EDS (Energy Dispersive X-ray Spectroscopy) and SEM (Scanning Electron Microscopy) images were obtained on a JEOL JSM-76OOF Scanning Electron Microscope. The single-point BET area was calculated using a Quadrasorb Quantachrome Jr. analyzer. Nitrogen adsorption/desorption isotherms at $P/P_0 = 0.1$ were determined at 290 K. Column chromatography was carried out on Merck silica gel 230−400 mesh. FAME profile analysis was acquired by the Ce 1–62 (AOCS 2005) and Solid Phase Microextraction (SPME) (PDMS/DVB/CAR fiber) methods, respectively, using an Agilent Technologies 7890A gas chromatograph equipped with DB-5 (60 m × 0.25 mm × 0.25 μm) column and coupled to an Agilent Technologies 5975C quadrupolar mass spectrometer, operated in mode electron impact ionization (70 eV). A comparison of the mass spectra with the NIST/EPA/NIH Mass Spectra Library (Positive identification: 80%) base data was made. The FAME retention times were compared to those obtained for chemical standards (37 component FAME mix, Supelco) injected into the gas chromatograph under the same experimental conditions. The heat of combustion of the FAME mixture was determined in a Parr 6725 semi-microcalorimeter equipped with an oxygen bomb model 1109A (22 mL capacity), electronic high-precision thermometer (Parr 6772, resolution ± 0.0001 °C), and a stirrer motor module operating at 450 rpm.

2.2 Plant Source and Ligand Isolation

Perymenium buphthalmoides DC. specimens were collected during the flowering stage on July 24, 2020, near km 3.5 of Tiripetio–Eréndira road, Michoacán state, Mexico (19° 30.9160´ N, 101° 20.6340´ W). A voucher specimen (00243995) is deposited at the Herbarium of Instituto de Ecología, A. C., Pátzcuaro, Michoacán, Mexico. As reported, kaurenoic acid and beyerenoic acid were isolated from *P. buphthalmoides* [22].

2.3 Synthesis and Characterization of Zn-diterpene Complexes **1** and **2**

Complexes **1** and **2** were synthesized using kaurenoic acid and beyerenoic acid as ligands and $ZnCl_2$ as the metal source as follows [22]: Solutions of beyerenoic acid or kaurenoic acid in CH_3OH-H_2O (1:1) (10 mL) were separately treated with NaOH (0.33 mmol, 100 mg) for 2 h at 25 °C. Subsequently, an aqueous solution of $ZnCl_2$ (0.165 mmol, 22.5 mg/5 mL) was added. The mixture was stirred for 5 h at 25 °C, evaporated under reduced pressure, and washed with hexanes, yielding white crystals in each case. Crystallization of **1** and **2** was achieved by a lower evaporation process from CH_2Cl_2-CH_3CN (4:1) and CH_2Cl_2-$CHCl_3$-CH_3OH (1:1:1) solvent mixtures, respectively. Compound **1**: White crystals, yield: 80%. *Anal. Calcd.* for $C_{120}H_{174}O_{13}Zn_4 \cdot 2C_6H_{14}$: C 70.20, H 9.01%; Found: C 70.83, H 8.97%. IR, ^{1}H, and ^{13}C NMR data (see supplementary material) agree with published values [22]. Compound **2**: White crystals, yield: 96%. *Anal. Calcd.* for $C_{120}H_{174}O_{13}Zn_4 \cdot 1.5C_6H_{14}$: C 69.94, H 8.87%; Found: C 69.83, H 8.87%. IR, ^{1}H, and ^{13}C NMR data (see supplementary material) agree with published values [22].

Thermal stability of **1** and **2** was determined by thermogravimetric analysis (TGA). For this purpose, 8.5 mg of **1** or **2** was placed into an aluminum crucible and allocated into the TGA chamber. The sample was then heated from 25 to 400 °C at 4 °C/min, under 20 mL/min of nitrogen (99.99%), which was kept constant during the experiment. Once at 400 °C, the sample was cooled to ambient temperature at 10 °C/min. The TGA experiments were performed in triplicate. The weight loss and energy profiles were acquired during the experiment.

2.4 Catalytic Experiments

Catalytic assays were carried out in a well-mixed stainless-steel Parr-5000 reactor. The reaction experiments were systematically performed at 120, 130, 140, 150, 160, or 170 °C, from 1 to 7 h, using 1 to 5 wt% of catalyst concerning oil and an oil/methanol ratio of 1:6, 1:10, 1:30, 1:50, or 1:100 (v/v). Initially, olive oil, methanol, and catalyst were charged into the reactor. Once the reactor was closed, the air was purged with nitrogen for 5 min and then pressurized with this gas to 2 bars to keep methanol in the liquid phase. The temperature rapidly increased to the selected temperature, and the stirring speed was set at 650 rpm. At the end of the experiment, the reactor was cooled down into an ice bath and depressurized. The catalyst was then removed from the reaction mixture by centrifugation, and the unreacted methanol was recovered from the reaction products by evaporation at 70 °C. The reaction products present two phases: fatty acid methyl esters (FAME) from the top layer and glycerol at the bottom. Both phases were separated by decantation. Subsequently, the phase containing FAME and methanol was evaporated using rotavapor. The FAME portion was dried over anhydrous Na_2SO_4, filtered, and finally analyzed by ^{1}H NMR and GC-MS. The energetic potential of FAME was also measured. All assays were performed in triplicate, and the average values are reported herein. A statistical analysis was also conducted. The reaction yields were determined according to Elkady *et al.* [32] as shown in Equation (1):

$$\text{Yield\%} = \text{FAME\% from GC analysis} \times \text{Volume yield} \quad (1)$$

where, Volume yield = (Volume of product/Volume of oil fed) × 100.

2.5 Statistical Analyses

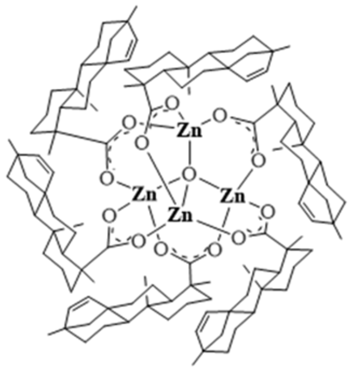
Numerical values are expressed as arithmetic means ±standard error of the mean (SEM). Data were evaluated with the GraphPad Prism®Version 6.00 software (GraphPad Software, Inc., San Diego, CA, USA). Statistical significance using the control assay was determined by the Student's test. The statistical significance of any difference in each parameter between groups was evaluated by one-way analysis of variance (ANOVA) followed by the Bonferroni test. The p values of < 0.001 were considered statistically significant.

3. Results and Discussion

The synthesis of the (μ_4-oxo)-hexakis(μ_2-beyerenate)-tetra-zinc(II) (**1**) and (μ_4-oxo)-hexakis(μ_2-kaurenate)-tetra-zinc(II) (**2**) was achieved as previously described, including crystallization procedure [22]. The obtention of **1** and **2** was validated by comparing the physical and spectroscopic data with a reference (see supplemental file, Figures S1-S10). Interestingly, these compounds contain six natural diterpene molecules and an oxo-tetrazinc core, favoring higher molecular symmetry by metalcore and relative lipophilicity adjudicated to terpene ligands [33], as depicted in Figure 1. Furthermore, the oxo-tetrazinc core seems to be a suitable catalyst for *O*-acylation reactions [34], and its catalytic performance could relate to the nature of ligands [28].

The thermodynamic stability was established by thermogravimetric analysis (TGA). Herein, the weight profiles indicate that both catalysts are stable from 25 to 200 °C, as shown in Figure 2. Weight loss of 11.6 wt% from 170-370 °C was noticed for compound **1**. Contrastingly, weight losses of 5.7 wt% at 170-235 °C and 2.3 wt% at about 235-350 °C were registered for catalyst **2**. This phenomenon can be related to occluded hexane used during the synthesis processes (see experimental section) because no significant weight loss was observed compared to the molecular weight in catalysts. As the TGA suggested, the solvent occlusion was more favored in compound **1** than in compound **2,** and it was congruent with the elemental analysis result (see experimental section).

The results indicated that a temperature range of 60 to 170 °C is optimal for conducting the transesterification reaction, as this range helps prevent the catalysts' decomposition. This study tested these derivatives as catalysts for the transesterification of methanol and olive oil, given that olive oil contains a balanced mixture of saturated and unsaturated fatty acids [36]. Our findings are summarized in Table 1.



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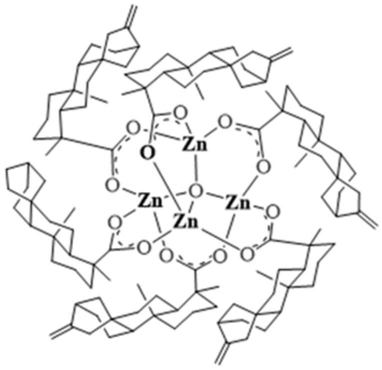

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Figure 1. Formulas of diterpene-Zn(II) complexes **1** and **2**.

In our previous research [35], we conducted an initial test using an oil-to-methanol ratio of 1:6 with 5 wt% of catalyst **1** at a temperature of 60 °C in an open vessel reactor. Under these conditions, we achieved a final yield of 28% after 6 hours of reaction (see Table 1, entry 1). The yield remained relatively unchanged when we increased the methanol ratio (entry 2). However, extending the reaction time to 12 hours (entry 3) increased yield to 37%.

In another experiment with an oil-to-methanol ratio of 1:50 (entry 4), we observed a transesterification yield of 41%, likely due to an enhancement in the interaction between the solvent and catalyst [25]. Conversely, when we added 10% THF [37] and 2 wt% of catalyst 1, the yield decreased to 34% after 12 hours (entry 5), suggesting that additives intended to improve solubility might have a detrimental effect.

By the above, the effect of the reaction temperature in the range of 120-170 °C was analyzed using 2 wt% of catalyst for 6 h, and methanol was used as the nucleophile and solvent (Table 1 entries 6-11) as in previous entries but increasing in a 1:100 (v/v) ratio. A suitable reaction temperature of 150 °C was found, which showed a transesterification yield of 95% (entry 9), confirming the need for the dual function of methanol [25]. Thus, results suggest that complex **1** can catalyst transesterification of robust molecules from complex mixtures as glycerides from natural sources, which deeply complements the catalytic potential of tetranuclear zinc clusters for transesterification [38]. Higher reaction temperatures (entries 10, 11) decrease the conversion, probably due to the decomposition of FAME [39].

The effect of the catalyst in the reaction medium was then studied from 1 to 5 wt% (entries 12-15). An increase in transesterification yield from 62 to 97% was noticed when augmenting the quantity of catalyst from 1 to 5 wt%. The effect of the reaction time was also addressed. As can be

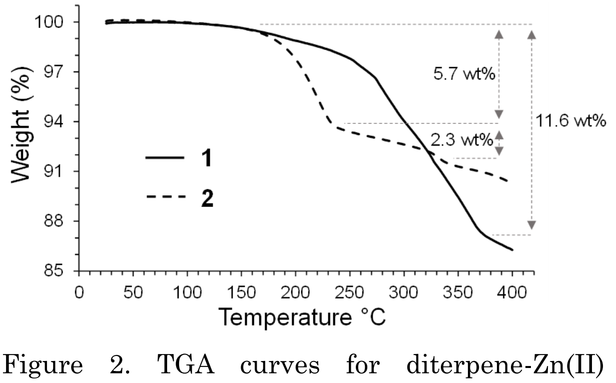

Figure 2. TGA curves for diterpene-Zn(II) complexes **1** and **2** range from 0–400 °C.

observed in Table 1, entries 16 to 21, a maximum transesterification yield of 97% was observed after five hours of reaction in the presence of catalyst **1**. At longer reaction times, the transesterification yield decreased, probably due to the transesterification of fatty acids with glycerol, as is commonly observed. Catalyst **2** was also tested in the transesterification of olive oil under these suitable experimental conditions. In this case, a FAME yield of 96% was observed, indicating similar reaction activity as that of catalyst **1**, which was expected since both compounds are alike.

The ^{1}H NMR data spectrum of the olive oil shows moiety signals at about δ 5.30-3.90 assigned to glycerate. The absence of these signals in the ^{1}H NMR spectrum of the reaction product and the appearance of a singlet at δ 3.56 attributed to FAME, as depicted in Figure 3, indicates the transesterification reaction and the proper purity of the process.

The analysis by gas chromatography coupled with mass spectrometry (GC-MS) showed 97.44%

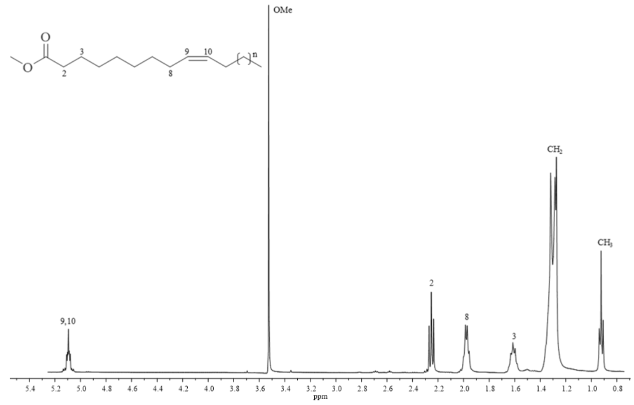

Figure 3. ^{1}H NMR spectra of FAME at 400 MHz in $CDCl_3$. The spectrum reveals the esterification of fatty acid mixtures and the purity of the product.

Table 2. FAME composition of transesterification product from olive oil using complex **1** as the catalyst.

FAME	GC-MS (wt%)
Oleic (C18:1)	62.47
Tridecanoic (C13:0)	22.50
Palmitoleic (C16:1)	8.61
Linolenic (C18:3)	1.34
Caprilic (C8:0)	0.48
Heptanoic (C7:0)	0.05
Pelargonic (C9:0)	0.04
15-Methylhexadecanoic (C17)	1.95
Total FAME	97.44

Table 1. Optimization of transesterification reaction using complex **1** as the catalyst. (Methanol plays the role of a nucleophile and a solvent. in 1:6 (oil:MeOH) proportion (v/v) for entry 1; 1:30 (v/v) for entries 2 and 3; 1:50 (v/v) for entry 4; 1:10:1 (oil:MeOH:THF) (v/v/v) for entry 5; 1:100 (v/v) for entries 6-21.)

Entry	Catalyst (wt%)	Temperature (°C)	Time (h)	FAME Yield (%)
1	5	60	6	28
2	5	60	6	27
3	5	60	12	37
4	5	60	12	41
5	2	60	12	34
6	2	120	6	15
7	2	130	6	40
8	2	140	6	26
9	2	150	6	95
10	2	160	6	72
11	2	170	6	73
12	1	150	6	62
13	3	150	6	80
14	4	150	6	80
15	5	150	6	97
16	2	150	1	19
17	2	150	2	53
18	2	150	3	72
19	2	150	4	82
20	2	150	5	97
21	2	150	7	84

of FAME composition. The oleic and tridecanoic acid methyl esters, among other FAME products, indicated partial fatty acid degradation, as described for several oil transesterifications [36, 40]. Other reaction products present in FAME are reported in Table 2. The heat of combustion assay of the FAME mixture showed a 33.72 MJ/kg value, which agrees with the reported data [41].

To establish a comparison of the catalytic potential of clusters **1** and **2**, the transesterification reaction conditions herein determined were also performed using ZnO as the catalyst since this compound could be considered as a proper analog of the catalysts **1** and **2** core, and the results are presented in Figure 4. Under the best experimental conditions for transesterification using **1** or **2**, ZnO showed a FAME yield of 16%, a much lower conversion, which agrees with other studies [42, 43]. This lower activity indicates the need for harsh reaction conditions to improve the conversion. Some additional research works recommend using adjuvants to enhance the catalytic activity of ZnO [44], which probably promotes the obtention of activated Zn-coordinated analogs. Herein, the relative lipophilicity of ligands in **1** and **2** could play a strategic role in gaining the catalyst core's affinity to the molecule target.

In line with this observation, the present research indicates that improving the catalytic performance of Zn(II) with these natural diterpenes provides better availability of the catalytic active sites for apolar targets. Consequently, both prepared catalysts showed high FAME yields under the selected experimental conditions.

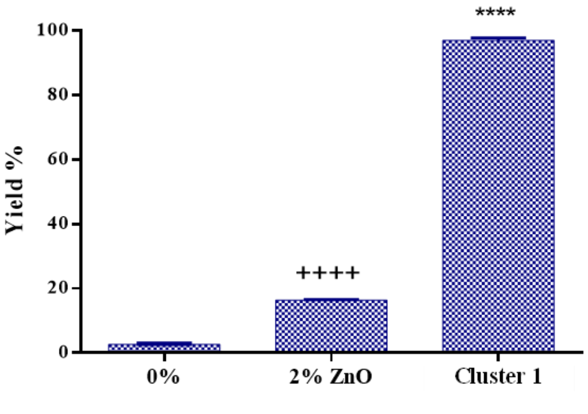

Figure 4. Comparison of catalytic performance of diterpene-Zn(II) complex **1** against ZnO or lack of catalyst in the transesterification reaction. Data are meant ±SEM from three independent experiments. The statistical significance of any difference in each parameter between groups was evaluated by one-way analysis of variance (ANOVA) followed by the Bonferroni test. ++++ $p < 0.001$, lack of catalyst (0%) vs. 2% ZnO; ****$p < 0.001$, 2% ZnO vs. 2% complex **1**; oil:methanol (1:100 v/v), 150 °C, 5 h.

It is good to mention that recovery of viable catalysts after the transesterification reaction was feasible at 53 ± 5%, which is intriguing since tetranuclear zinc cluster analogs provide homogeneous catalysis [25,45,46]; consequently, this topic was boarded using catalyst **1**. Spectroscopic data (IR, NMR) revealed the apparent chemical stability of the recovered solid catalyst. Furthermore, an XRD analysis (Figure 5) of crystallized compound **1** before its being used in the catalytic process (Figure 5a) showed a crystalline pattern with main peaks at θ of 10.2, 10.3, 11.8, 14.4, 14.5, 15.6, 16.7, 17.7, and 23.6. After the reaction, the XRD analysis of **1** (Figure 5b) revealed the presence of main peaks at θ 12.5, 15.8, 16.3, and 17.7. The sharpness of the peaks in these samples suggested higher crystallinity than that observed in XRD analysis of not crystallized catalyst **1** before its use in the catalytic process, whose broad peaks at θ 10.1, 10.8, 14.6, 15.0, 15.5, 16.5, and 16.7 highlighted (Figure 5c). Each process results in unique and complex crystalline structures that occupy varying distributions and angular ranges. It is important to note that it was impossible to identify any substances in the latest PDF database using indexing.

These results imply the formation of new crystalline structures during catalysis that could be associated with novel and mixed Zn-clusters formed through the catalytic process; thus, cluster

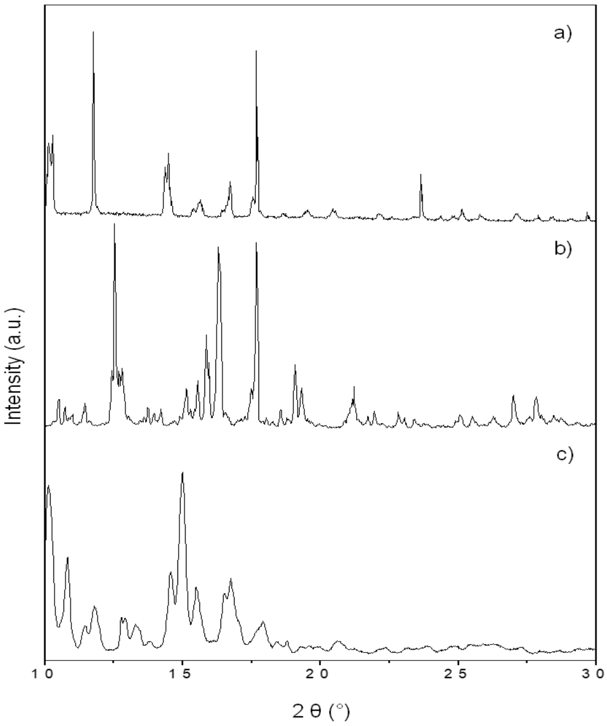

Figure 5. Results of XRD analysis of compound **1** (a) before being used as the catalyst, (b) recovered from the catalysis process, and (c) uncrystallized catalyst.

collapses into trinuclear, binuclear, or mononuclear complexes or even higher-nuclear species with or without catalytic potential can occur as the literature referred [47]. However, it is good to highlight that the recrystallization process of the recovered solid catalyst provided the expected spectral data (NMR and IR) for **1**, including the melting point datum [22]. Furthermore, this catalyst was immediately recycled to provide transesterification in 80% yield and a catalyst recovery of 30%. We attribute this yield decrease to the diminished batching in the assay. These results show that diterpene-Zn complexes **1** and **2** should be considered heterogeneous/homogeneous catalysts as observed in ZnO nanostructures [48]. Interestingly, the catalyst from Figure 5c provided competitive transesterification yields (93%) but complete leaching, suggesting that crystallinity is a critical property in these catalysts to diminish or avoid leaching. Our research is addressing this phenomenon.

Figures 6a and 6b display SEM images of the material particles before and after the catalysis process. The initial structure had low crystallinity, as suggested by the amorphous particles observed in the image, whose particle size is heterogeneous. However, certain crystalline facets appeared after crystallization, indicating increased crystallinity, forming prisms with wide-ranging crystal growth patterns. Despite these changes, the chemical composition of the main elements remained constant, as confirmed by EDS spectroscopy (Figure 6c and d), suggesting structural phase transformations. It is good to mention that the single point BET area for compound **1** was 2.0 m^2/g, while 0.7 m^2/g was determined for compound **2** when crystalline forms of both catalysts were tested.

The BET and SEM results are congruent with the catalytic results since the catalysts **1** and **2** are faceted, which may enhance their surface activity. Moreover, the material demonstrates relatively high catalytic activity under specific reaction conditions. It has been reported that in transesterification reactions, a catalyst with a low surface area can still exhibit high catalytic activity [49,50]. The catalytic behavior is attributed to the Lewis acid sites, which play a crucial role in the catalytic activity, particularly in the presence of methanol, as presented in this work.

Based on the experimental results, a proposed mechanism for transesterification reaction in the presence of compounds **1** or **2** as catalysts is didactically illustrated in Figure 7. The scheme is divided into six main stages (**I**-**VI**). Chemical recognition of a carbonyl group from the triglyceride on Zn^{2+} from the catalyst is considered (**I**) [51]. Consequently, the carbonyl group is activated, and a nucleophilic attack with methanol can occur (**II**). The subsequent migration of a proton from methanol to the adjacent oxygen atom of the coordinated glycerol

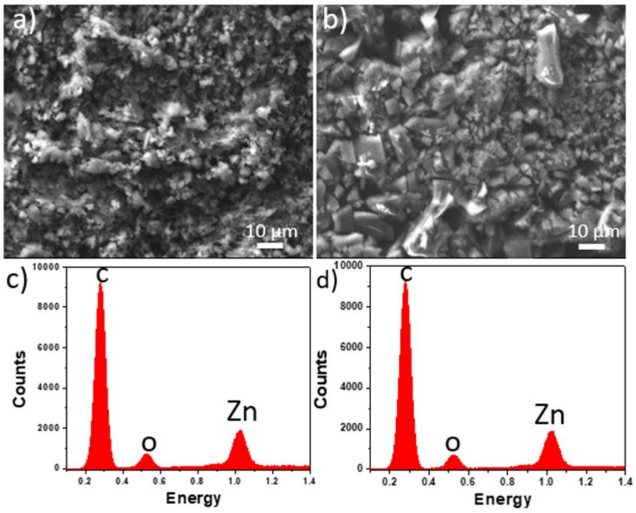

Figure 6. SEM analysis of compound **1** (a) uncrystallized catalyst (b) after being used as the catalyst. The elemental composition of (c) compound **1** (C 66.44, O 31.23, Zn 2.33) and (d) compound **2** (C 66.20, O 31.03, Zn 2.77).

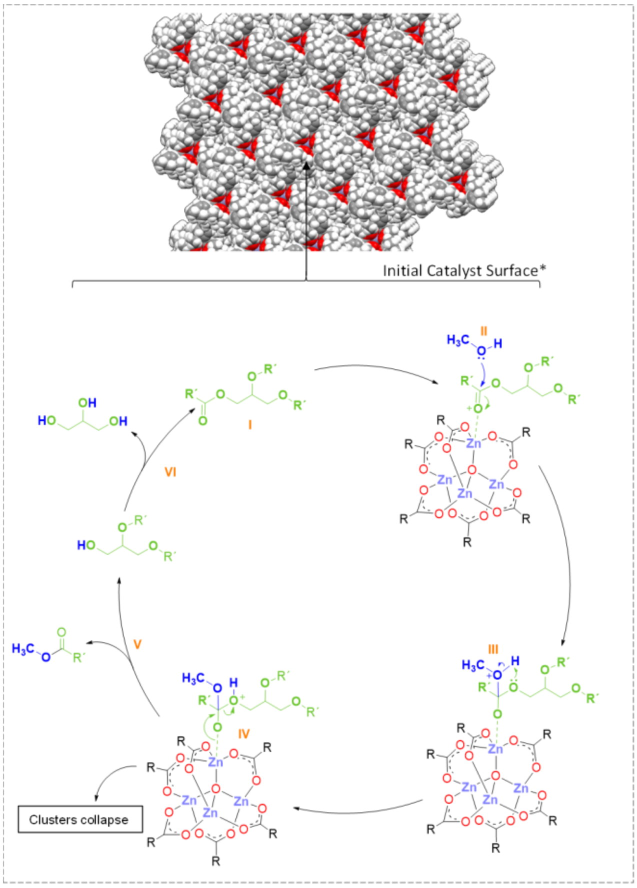

Figure 7. Proposed reaction mechanism for the transesterification of olive oil with methanol in the presence of compounds **1** or **2** as the catalysts. *The catalyst surface simulated from the cif file CCDC 1527715.

ester occurs (**III**), thus promoting an electronic rearrangement that favors the breaking of the metal-O chemical bond (**IV**), generating FAME and the corresponding glyceride derivative (**V**) [52]. The catalytic cycle could continue with the yielded glyceride (**VI**) to gain the corresponding monoglyceride, which finally yields glycerol after catalysis [53]. Alternatively, the catalytic process could continue activating a new triglyceride molecule (step I). A simple simulation of the catalyst surface from the cif file (CCDC 1527715) warns that, at most, one of the four Zn atoms in the cluster from the surface can participate in the reaction. The catalyst collapse during transesterification is not discarded, promoting lower-nuclear or higher-nuclear species with or without capability for catalytic activity.

4. Conclusions

The catalytic profile of diterpene-Zn(II) compounds is herein reported. These compounds exhibit heterogeneous/homogeneous catalytic potential in transesterification reactions using a vegetal oil source with acceptable yields despite the lower surface area; notwithstanding, both catalysts are faceted in the crystalline form, which probably enhances the surface activity. The observed purity of the reaction products (FAME and glycerin) suggests these catalysts are well-matched with transesterification reactions. To our knowledge, diterpene-Zn(II) catalysts have not been used previously for catalytic purposes. These natural compounds could be promising for synthesizing new catalysts compatible with apolar and robust substrates. Attractive facts about these types of catalysts involve facile synthesis, crystallinity, and efficient catalysts under relatively mild conditions. Although high transesterification yields were obtained in our study, the lixiviation occurs as described for several heterogeneous catalysts and needs to be addressed. In addition, a phytochemical march is required for ligand acquisition if only natural sources are available; fortunately, several diterpene compounds are commercially offered. Notwithstanding, a higher molecular diversity could be obtained from plants, which could be chemically improved by coordination chemistry and used for catalytic purposes, thus representing a new hopeful class of sustainable catalysts, as demonstrated herein.

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CRedit Author Statement

Authors contribution: M.A. Martínez-Torres, Validation, Methodology, Formal analysis; A. Talavera-Alemán: Validation, Methodology, Formal analysis, Conceptualization; K. Zamudio-Jaime, Validation, Methodology, Formal analysis; A.K. Villagómez-Guzmán: Resources, Methodology, Data curation; L. Quevedo-Tinoco: Resources, Methodology, Data curation; J.L. Rico: Supervision, Project administration, Funding acquisition, Formal analysis, Conceptualization; G. Rosas: Supervision, Project administration, Funding acquisition, Formal analysis, Conceptualization; R.E. del Río: Visualization, Supervision, Project administration, Investigation, Formal analysis, Conceptualization; M.A. Gómez-Hurtado: Writing - Original Draft, Writing - Review & Editing, Supervision, Project administration, Investigation, Funding acquisition, Formal analysis, Conceptualization; G. Rodríguez-García: Writing – review & editing, Supervision, Funding acquisition, Conceptualization. All authors have read and agreed to the published version of the manuscript.

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