





Article

Catalytic Activity of New Oxovanadium(IV) Microclusters with 2-Phenylpyridine in Olefin Oligomerization

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Abstract: So far, few microclusters containing vanadium have been described in the literature. In this report, the synthesis protocol for the preparation of oxovanadium (IV) microclusters with 2-phenylpyridine is shown for the first time. Moreover, the crystal structure of these microclusters is also studied through the use of X-rays. The morphology of the prepared crystals is investigated using a field-emission Scanning Electron Microscope (SEM). The new compound, after activation by modified methylaluminoxane as the catalytic system, is investigated regarding the oligomerizations of 3-buten-1-ol, 2-chloro-2-propen-1-ol, allyl alcohol, and 2,3-dibromo-2-propen-1-ol. The products of oligomerization are tested by the TG-FTIR and MALDI-TOF-MS methods. Moreover, the values of catalytic activities for the new oxovanadium(IV) microclusters with 2-phenylpyridine are determined for the 3-buten-1-ol, 2-chloro-2-propen-1-ol, allyl alcohol, and 2,3-dibromo-2-propen-1-ol oligomerizations. Oxovanadium(IV) microclusters with 2-phenylpyridine are shown to be very highly active precatalysts for the oligomerization of allyl alcohol, 2,3-dibromo-2-propen-1-ol, and 3-buten-1-ol. However, in the case of 2-chloro-2-propen-1-ol oligomerization, the new microclusters are seen as highly active precatalysts.

Keywords: oxovanadium(IV) complex; 2-phenylpyridine; oligomerization; 2-chloro-2-propen-1-ol; allyl alcohol; 3-buten-2-ol



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1. Introduction

The metathesis of olefin has been known and used in organic synthesis since the middle of the twentieth century [1,2]. The first example described was the polymerization of norbornene carried out at Du Pont during research on extending the scope of applications of Ziegler-type polymerization [3–5]. In 1968, Calderon et al. were the first to use the term “olefin metathesis” [6]. The high synthetic potential of this reaction has remained untapped for years. Initially, the following systems were used as catalysts: $\text{TiCl}_4/\text{AlEt}_3$, $\text{MoCl}_5/\text{AlEt}_3$, and $\text{WCl}_6/\text{AlEt}_3$ [7]. Due to their low cost and simple synthesis, they have played an important role in the industrial use of olefin metathesis—e.g., in the Shell Higher Olefin Process (SHOP) [8]. These have allowed for the efficient course of ring-opening metathesis polymerization (ROMP) and cross-metathesis (CM). However, their usefulness has been limited due to the need for high temperatures and strong Lewis acids. There are the following types of metathesis: Cross Metathesis (CM) [9,10], Ring Closing Metathesis (RCM) [11], and Ring Opening Metathesis (ROM) [12]. In addition, a very important place in the industry is occupied by: Ring Opening Metathesis Polymerization and Acyclic Diene Metathesis (ADMET) polymerization. The synthesis of new, stable complex compounds catalyzing the olefin oligomerization and polymerization reaction,

as well as proposing their mechanisms, is a challenge for the next generation of scientists. Many catalytic systems, both homogeneous and heterogeneous, can be used to initiate olefin metathesis [13]. These systems are based on transition metals containing incompletely filled 3D, 4D, or 5D orbitals, such as chromium, vanadium, cobalt, rhenium, or titanium. The use of well-defined catalysts is required in order to obtain compounds of a desired, well-defined structure. These catalysts should be sufficiently stable to be characterized by spectroscopic and X-ray structure methods, and should allow for the control and observation of the formed intermediate products [14]. In turn, the functional groups present in the substrate, as well as the oxygen present in the atmosphere or the environment—e.g., water present in the reaction system—may influence the activity of the catalysts. These factors can react with the active center of the metal, resulting in a partial or complete loss of catalytic properties [15]. They can also compete with the double bond in coordination to the metal ion. Therefore, the reactants used in these reactions must not have functional groups for which the catalyst has a higher affinity than the carbon–carbon double bond. Therefore, mainly organic compounds are used as ligands—e.g., pyridine, lactones, proline derivatives, quinoline, 2,2'-bipyridine, pyrazine, or organophosphorus compounds [16–22].

The aim of this article is twofold. The first is the development of a synthesis protocol for the preparation of a catalytic system containing oxovanadium(IV) microclusters with 2-phenylpyridine. Secondly, it attempts to optimize the obtained catalytic system, and subsequently to use this system in the olefin oligomerization reaction. The novelty of this work is the synthesis and characterization of the new coordination compound—i.e., oxovanadium(IV) microclusters with 2-phenylpyridine—and, for the first time, the catalytic activity of these microclusters have been investigated for the oligomerization of the following olefins: allyl alcohol, 2,3-dibromo-2-propen-1-ol, 3-buten-1-ol, and 2-chloro-2-propen-1-ol.

2. Materials and Methods

2.1. Materials

The reagents used for the synthesis of oxovanadium(IV) microclusters with 2-phenylpyridine were as follows: vanadyl acetylacetonate (98% purity), oxydiacetic acid (98% purity), and 2-phenylpyridine (98% purity). All reagents were purchased from Sigma-Aldrich (St. Louis, MO, USA).

The olefins 3-buten-2-ol (97% purity), 2-chloro-2-propen-1-ol (90% purity), allyl alcohol (98.5% purity), and 2,3-dibromo-2-propen-1-ol (90% purity) were purchased from Merck, Darmstadt, Germany. The modified methylaluminoxane MMAO-12 (7 wt.%) aluminum in toluene was purchased from Merck.

2.2. Syntheses

The synthesis procedure of oxovanadium(IV) microclusters with 2-phenylpyridine was as follows:

Mix vanadyl acetylacetonate $\text{VO}(\text{acac})_2$ (2.65 g), H_2oda (oxydiacetic acid) (1.34 g), and 2.86 mL (0.02 mol) of 2-phenylpyridine, then add 50 mL of water. Boil everything until the solution changes color. The mixture should be refluxed at 100 °C for 2 h. After one month, a new compound was obtained in the form of crystals.

The selected olefins, 3-buten-2-ol, 2-chloro-2-propen-1-ol, allyl alcohol, and 2,3-dibromo-2-propen-1-ol (purchased from Merck), were subjected to oligomerization processes at nitrogen atmosphere, atmospheric pressure, and 65 °C. In the first step, solutions containing 3 μmol of the synthesized complex, 1 mL of toluene, and 1 mL of DMSO were prepared in a glass cell. In the next step, 3 mL of modified methylaluminoxane (MMAO-12, 7 wt.% aluminum in toluene—purchased from Merck) was slowly added into the cell. Next, 1 mL of 3-buten-2-ol, 2-chloro-2-propen-1-ol, allyl alcohol, and 2,3-dibromo-2-propen-1-ol, respectively, were added into the mixture of oxovanadium(IV) microclusters with 2-phenylpyridine activated with modified methylaluminoxane. The solution of each olefin was stirred until a gel was formed.

2.3. Physicochemical Characteristics

Diffraction data were collected on an Oxford Diffraction Gemini R ULTRA Ruby CCD diffractometer ($T = 295(2)$ K, $\text{MoK}\alpha$ ($\lambda = 0.71073$ Å) radiation, Table 1) and were reduced using the CrysAlis RED software (ver. 1.171.41.16a) [23]. The structures were refined and solved using the SHELX package (ver. 2017/1) [24]. H-atoms from water molecules were located on a difference Fourier map and refined using restraints (DFIX command) of $d_{(\text{O-H})} = 0.95$ Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$, whereas H-atoms bound to N-atoms were located on a difference Fourier map and refined freely. H-atoms bound to C-atoms were placed geometrically and refined using a riding model of $d_{(\text{C-H})} = 0.93$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. All interactions were identified using the PLATON program (ver. 181115) [25].

Table 1. Crystal data and structure refinement for the title compound.

Chemical Formula	$\text{V}_{20}\text{C}_{121}\text{H}_{123}\text{N}_{11}\text{O}_{62}$
Formula weight/ $\text{g}\cdot\text{mol}^{-1}$	3742.10
Crystal system	monoclinic
Space group	$P2_1/c$
$a/\text{Å}$	15.2074(5)
$b/\text{Å}$	18.4168(6)
$c/\text{Å}$	24.2763(7)
$\alpha/^\circ$	90
$\beta/^\circ$	91.304(3)
$\gamma/^\circ$	90
$V/\text{Å}^3$	6797.4(4)
Z	2
T/K	293(2)
$\lambda_{\text{Mo}}/\text{Å}$	0.71073
$\rho_{\text{calc}}/\text{g}\cdot\text{cm}^{-3}$	1.828
$F(000)$	3762
μ/mm^{-1}	1.403
θ range/ $^\circ$	3.32–25.00
Completeness $\theta/\%$	99.8
Reflections collected	53,867
Reflections unique	11,941 [$R_{\text{int}} = 0.1078$]
Data/restraints/parameters	11,941/6/1011
Goodness of fit on F^2	1.037
Final R_1 value ($I > 2\sigma(I)$)	0.0639
Final wR_2 value ($I > 2\sigma(I)$)	0.0824
Final R_1 value (all data)	0.1275
Final wR_2 value (all data)	0.0968
CCDC number	2,117,153

The ORTEPII [26], PLUTO-78 [27], and Mercury (ver. 2020.2.0) [28] programs were used to prepare the molecular graphics. Full crystallographic details for the title compound have been deposited in the Cambridge Crystallographic Data Center (deposition No. CCDC 2117153) and they may be obtained from the link: <http://www.ccdc.cam.ac.uk> (date of access 20 September 2021), via e-mail: deposit@ccdc.cam.ac.uk, or through The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK.

The MALDI-TOF-MS spectra of oligomerization products were recorded using 2,5-Dihydroxybenzoic acid (DHB) as a matrix. The studies were conducted on a Bruker Biflex III spectrometer.

The TG-FTIR thermogravimetric analysis of oligomerization products was conducted on TG209 Thermometer (Netzsch). All samples were investigated in the temperature range 20–1000 °C.

The morphology of the prepared clusters was investigated using a field-emission Scanning Electron Microscope (SEM). For sample preparation, a certain amount of the

powder was deposited onto carbon tape and were imaged with JEOL JSM-7610 F operating at 15 kV.

3. Results and Discussion

The title compound was found to crystallize in the monoclinic $P2_1/c$ space group with one $[V_{10}O_{28}H_2]^{4+}$ cluster, four 2-phenylpyridine cations, one and a half 2-phenylpyridine molecules, and three water molecules in the asymmetric unit (Figures 1 and 2, Table 1). In the crystal of the title compound neighboring $[V_{10}O_{28}H_2]^{4+}$ clusters interacted through $O_{(cluster)}-H\cdots O_{(cluster)}$ hydrogen bonds to form centrosymmetric dimers (Figure 2b, Table 2). The adjacent dimers were connected directly via short $O\cdots O$ contact ($d_{(O18\cdots O18)} = 2.90 \text{ \AA}$) and indirectly through water molecules via $O_{(water)}-H\cdots O_{(cluster)}$ hydrogen bonds to produce tapes along ab -plane (Figure 2c, Table 2). These tapes are linked by $N_{(pyridine)}-H\cdots O_{(cluster)}$, $C_{(pyridine)}-H\cdots O_{(cluster)}$ hydrogen bonds, and π - π interactions in which one 2-phenylpyridine molecule and one 2-phenylpyridine cation were engaged to create layers along a -axis (Figures 2d,e and 3). The π -stacked columns formed by one 2-phenylpyridine molecule and three 2-phenylpyridine cations were connected with these layers via strong $N-H\cdots O_{(water)}$, $O_{(water)}-H\cdots O_{(cluster)}$, and $O_{(water)}-H\cdots N_{(pyridine)}$ hydrogen bonds and weak $C_{(pyridine)}-H\cdots O_{(cluster)}$ hydrogen bonds to form a 3D framework structure (Figure 3, Table 2).

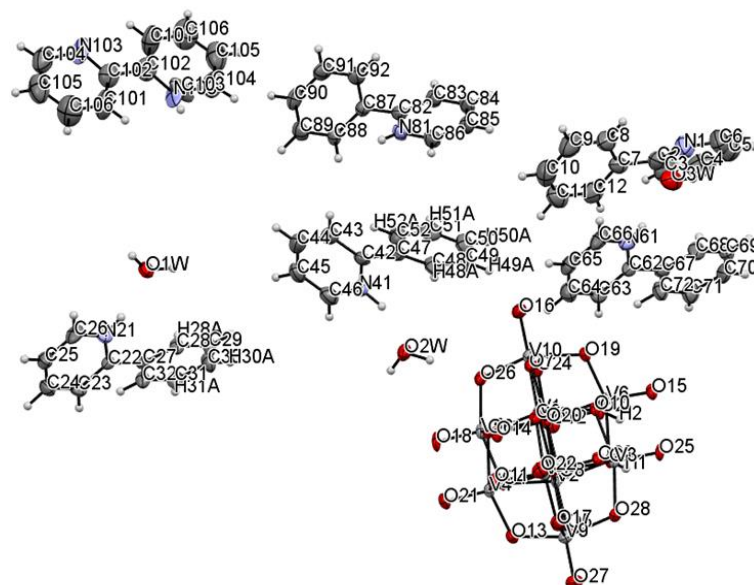


Figure 1. Molecular structure of title compound, showing the atom-labelling scheme.

Table 2. Hydrogen bond geometry for the title compound.

D–H \cdots A	d(D–H) [Å]	d(H \cdots A) [Å]	d(D \cdots A) (Å)	\angle D–H \cdots A (°)
O1–H1 \cdots O15 ⁱ	0.75(2)	2.03(5)	2.745(5)	175(7)
O1W–H1WA \cdots O6	0.94(2)	2.01(3)	2.908(5)	158(4)
O2–H2 \cdots O25 ⁱ	0.80(7)	2.05(7)	2.810(5)	159(6)
O1W–H1WB \cdots O18 ⁱⁱ	0.92(4)	2.01(4)	2.910(5)	164(5)
O2W–H2WA \cdots O21 ⁱⁱⁱ	0.93(4)	1.99(5)	2.881(5)	161(5)
O2W–H2WB \cdots O26 ^{iv}	0.93(3)	1.88(3)	2.807(5)	172(5)
O3W–H3WA \cdots O11 ^v	0.95(5)	2.08(6)	3.899(6)	144(4)
O3W–H3WA \cdots O21 ^v	0.95(5)	2.37(5)	2.160(6)	141(4)
O3W–H3WB \cdots N1	0.93(4)	2.03(5)	2.910(7)	158(6)
N21–H21A \cdots O1W	0.87(5)	1.86(5)	2.718(6)	166(5)
N41–H41A \cdots O2W	0.98(5)	1.77(5)	2.697(6)	156(5)
N61–H61A \cdots O3W	0.76(5)	1.99(5)	2.699(7)	158(5)
N81–H81A \cdots O28	0.80(5)	2.05(5)	2.831(6)	167(5)
C23–H23A \cdots O23 ^{vi}	0.93	2.51	3.334(6)	148

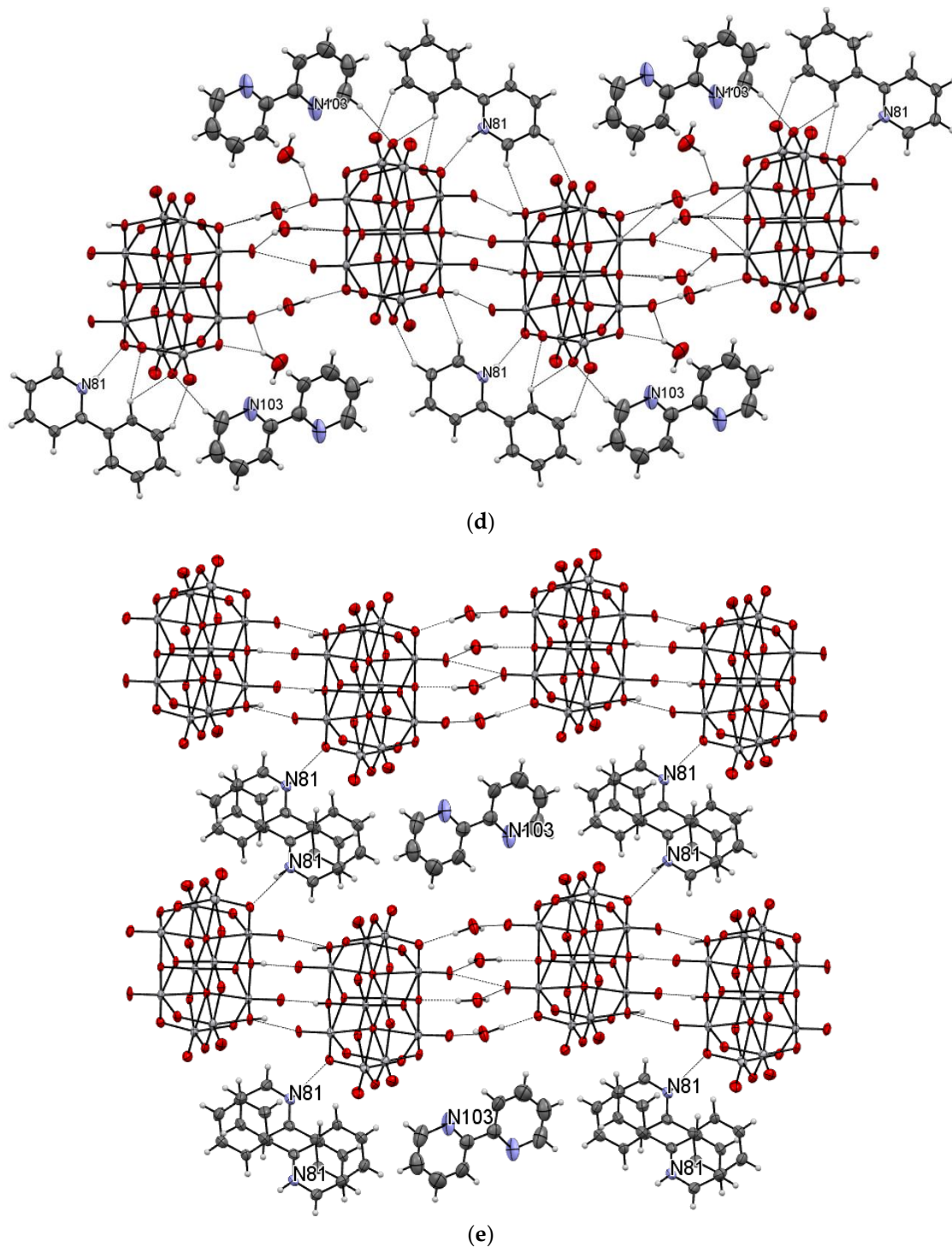


Figure 2. Self-assembly of $[V_{10}O_{28}H_2]^{4-}$ cluster (hydrogen bonds are represented by dashed lines); (a–e) panels exhibit various fragments of new oxovanadium(IV) microclusters with 2-phenylpyridine.

The field emission SEM images of the particles are shown in Figure 4a–c. SEM is the most widely used technique for characterizing the nanomaterials in terms of physical morphology of the particles. The morphology of the obtained crystals is irregular with a smooth surface. The bigger particle sizes range from 1 to 4.5 μm . It can be noticed that part of the structure has smaller particles, with some sizes of around 0.5 μm . The average size distribution (diameter) of oxovanadium(IV) microclusters with 2-phenylpyridine was calculated from the statistically average sizes of 100 nanoparticles (Figure 4d). No aggregate formation was observed.

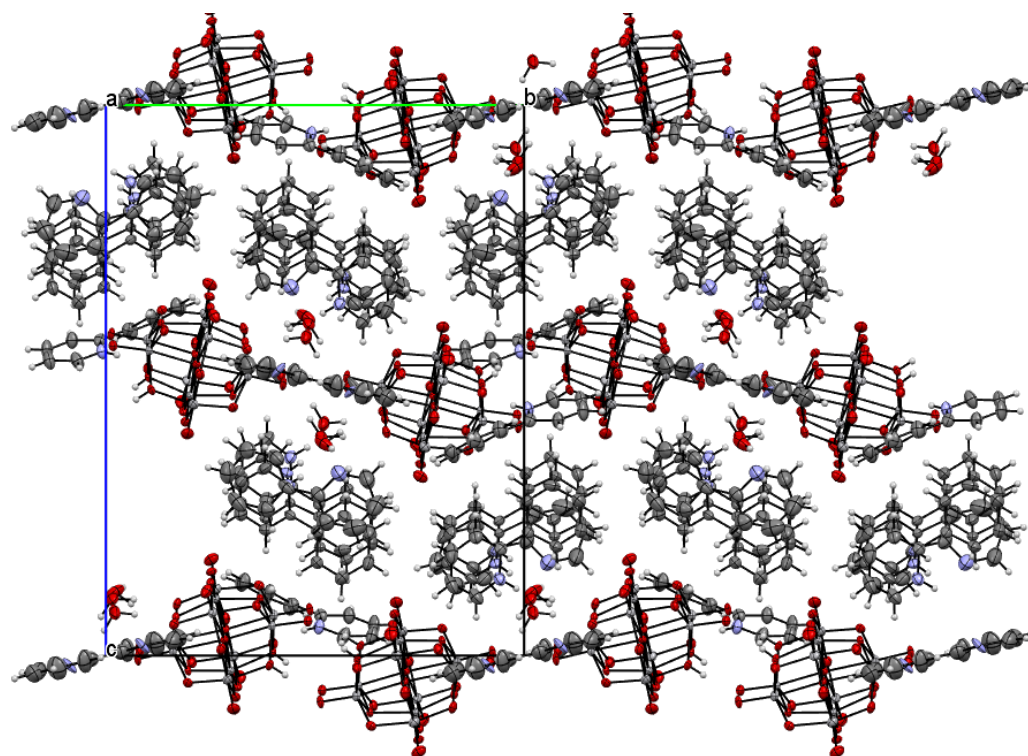


Figure 3. Crystal packing of title compound viewed along the *a*-axis.

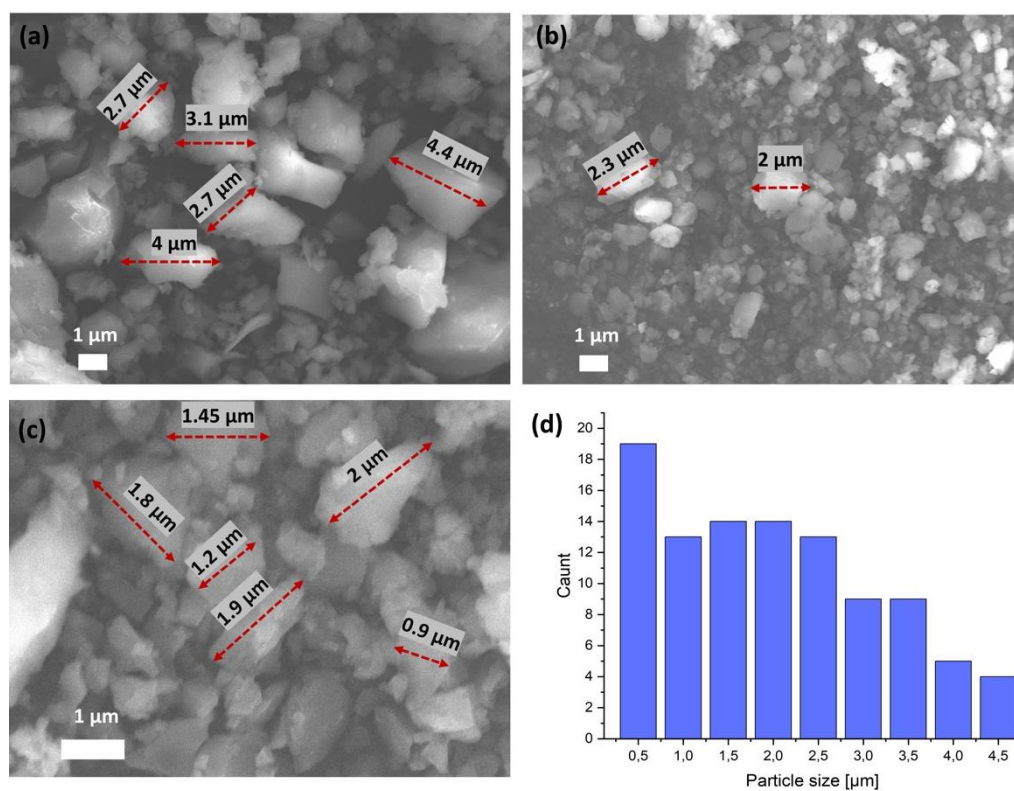


Figure 4. (a–c) SEM images and (d) average size distribution of oxovanadium(IV) microclusters with 2-phenylpyridine.

In this report, for the first time new oxovanadium(IV) microclusters with 2-phenylpyridine have been used as precatalysts in the oligomerization processes of olefins such as 3-buten-1-ol, 2-chloro-2-propen-1-ol, allyl alcohol, and 2,3-dibromo-2-propen-1-ol. All oligomer-

ization processes were carried out under a nitrogen atmosphere, atmospheric pressure, and temperature of 65 °C. The obtained products from the oligomerization of all the tested olefins, 3-buten-1-ol, 2-chloro-2-propen-1-ol, allyl alcohol, and 2,3-dibromo-2-propen-1-ol, were subjected to TG-FITR and MALDI-TOF-MS tests. The results obtained by the TG-FITR method are shown in Figure 5. For all oligomerization products, water, CO₂, and CO were released during thermal decomposition. It should be noted, however, that in the case of the oligomers of 2,3-dibromo-2-propen-1-ol, the amounts of water volatilized were insignificant. The oligomerization products of 2,3-dibromo-2-propen-1-ol, during thermal decomposition, after more than 1 h of measurement released HBr. Samples of 3-buten-1-ol oligomers and oligomers of allyl alcohol were characterized by the release of methane after 50 min of measurement. It is worth noting that 2,3-dibromo-2-propen-1-ol oligomers differed in their behavior in the temperature regime from other oligomers. This may be due to the high amount of bromine in the oligomer chain.

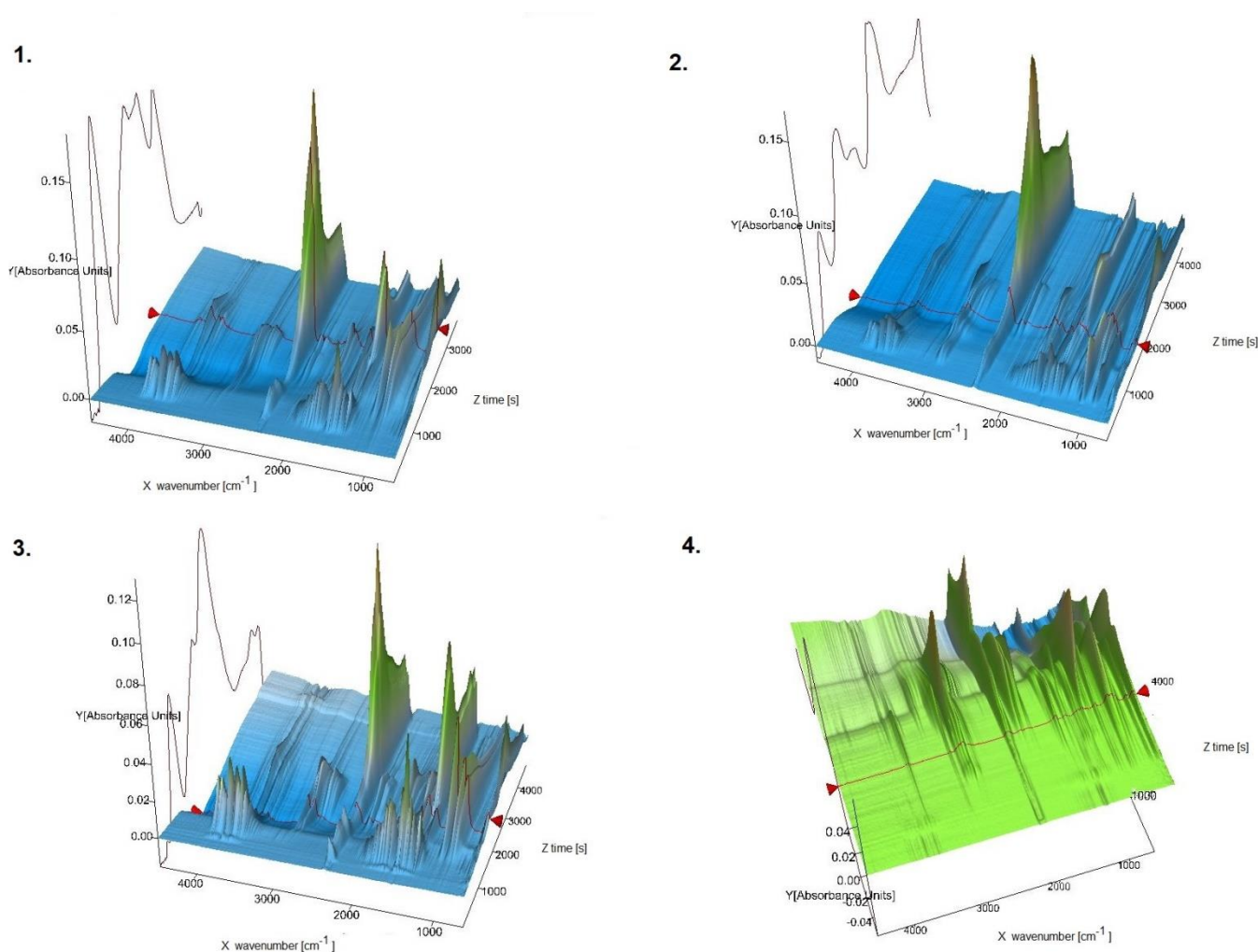


Figure 5. TG-FITR spectra (3D) for 1—oligomers of 3-buten-1-ol; 2—oligomers of 2-chloro-2-propen-1-ol; 3—oligomers of allyl alcohol; 4—oligomers of 2,3-dibromo-2-propen-1-ol.

The test results obtained by the TG-FITR method show that the oligomers of 3-buten-1-ol, 2-chloro-2-propen-1-ol, allyl alcohol, and 2,3-dibromo-2-propen-1-ol consist of oligomer chains with a different content of mers; from 3 in the case of 2,3-dibromo-2-propen-1-ol to 17 mers in the case of allyl alcohol. Oligomeric chains composed of the largest number of mers were obtained using allyl alcohol as the monomer. Thus, a mixture of oligomers consisting of 17, 14, and 11 mers was obtained. The oligomerization of 3-buten-1-ol led to a chain sequence with 16, 14, 12, and 9 mers. In the case of the oligomerization of

2-chloro-2-propen-1-ol, chains of 14, 13, 11, 9, and 7 mers were obtained. A distinctive case was the oligomerization of 2,3-dibromo-2-propen-1-ol, which resulted in the lowest number of mers—i.e., 5, 4, and 3—occurring in the oligomer chains.

These studies on the catalytic activity of new oxovanadium(IV) microclusters with 2-phenylpyridine determined the values of catalytic activity for the compounds formed from the oligomerization of four different olefins: 3-buten-1-ol, 2-chloro-2-propen-1-ol, allyl alcohol, and 2,3-dibromo-2-propen-1-ol. The calculated catalytic activities are as follows in Table 3.

Table 3. Data for the oligomerizations of selected olefins using new oxovanadium(IV) microclusters with 2-phenylpyridine activated by MMAO-12.

Entry	Olefin	Amt of V (μmol)	t (min)	Molar Ratio Compound: MMAO	Activity ($\text{g}\cdot\text{mmol}^{-1}\cdot\text{h}^{-1}$)
1	3-buten-1-ol	3	35	1:1000	2571
2	2-chloro-2-propen-1-ol	3	28	1:1000	643
3	allyl alcohol	3	29	1:1000	3724
4	2,3-dibromo-2-propen-1-ol	3	25	1:1000	3096

Based on the adopted division of catalytic efficiency introduced in 1999 by Britovsek, Gibson, and Wass [29], the following conclusions can be drawn. The calculated catalytic activities prove that the new microclusters are highly active precatalysts for the oligomerizations of 3-buten-1-ol, allyl alcohol, and 2,3-dibromo-2-propen-1-ol. Moreover, in the case of the oligomerization of 2-chloro-2-propen-1-ol, a new compound of oxovanadium(IV) with 2-phenylpyridine was discovered to be a highly active precatalyst.

4. Conclusions

In this report, we described for the first time the synthesis protocol for the preparation of oxovanadium(IV) microclusters with 2-phenylpyridin, and the catalytic activity of the new compound for the oligomerizations of 3-buten-1-ol, 2-chloro-2-propen-1-ol, allyl alcohol, and 2,3-dibromo-2-propen-1-ol. The synthesis of new microclusters was carried out using vanadyl acetylacetonate, oxydiacetic acid, and 2-phenylpyridine in water. The crystallographic studies confirmed that a $[\text{V}_{10}\text{O}_{28}\text{H}_2]^{4-}$ cluster forms centrosymmetric dimers by interacting with $\text{O}_{(\text{cluster})}-\text{H}\cdots\text{O}_{(\text{cluster})}$. A SEM analysis showed that the morphology of the obtained crystals were irregular with a smooth surface. The bigger particles sizes ranged from 1 to 4.5 μm . The oxovanadium(IV) microclusters with 2-phenylpyridine were used after activation by MMAO-12 as catalytic systems in the oligomerizations of 3-buten-1-ol, 2-chloro-2-propen-1-ol, allyl alcohol, and 2,3-dibromo-2-propen-1-ol. The products of oligomerization were tested by the TG-FTIR and MALDI-TOF-MS methods. TG-FTIR method showed that the oligomer samples obtained from selected olefins release CO, CO₂, and water. MALDI-TOF-MS data confirmed that all oligomers consist of chains with a different content of mers in the range of 3–17. This study shows the catalytic activities of oxovanadium(IV) microclusters with 2-phenylpyridine act, after activation by MMAO-12, as highly active catalytic systems for 3-buten-1-ol, allyl alcohol, and 2,3-dibromo-2-propen-1-ol, and that they exhibit highly active catalytic properties for 2-chloro-2-propen-1-ol oligomerization.

Author Contributions: Conceptualization: J.D., B.G., and D.J.; methodology: D.J., J.D., B.G. and A.M.; investigation: T.S., J.D., D.J., A.S., B.G., A.M.; writing—original draft preparation: J.D., D.J., A.S., A.M., B.G., writing—review and editing: J.D., D.J., A.M., P.K., B.G.; funding acquisition: B.G. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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