Catalysis Communications 142 (2020) 106041

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Biomimetic conversion of α-pinene with H_2O_2 to sobrerol over V_2O_5: Dihydroxylation by a peroxo vanadium peracid vectoring gentle synergistic oxidation

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ARTICLE INFO

Keywords:
Dihydroxylation
Sobrerol
V_2O_5
Hydrogen peroxide

ABSTRACT

In this communication, we report the gentle preparation of sobrerol from dihydroxylation of α-pinene synergistically catalyzed by V_2O_5-H_2O_2 under benign conditions. It was proposed that a “peroxo vanadium acid”, $V^{V}O(OH)(OOH)$, was formed by HOO^- insertion and proton transfer between V_2O_5 and H_2O_2. Theoretical DFT calculations that using the dimer-vanadium peracid as a model of the catalytically active species revealed that peroxo vanadium acid exhibited bifunctional catalytic capabilities resembling epoxidation of α-pinene by peracetic acid and then open-ring hydration with an acetic media.

1. Introduction

The excellent oxidative catalysis properties of vanadium pentoxide (V_2O_5) have been extensively recognized. It is widely known that V_2O_5 is the essential ingredient of industrial catalysts in the production of bulk chemical raw materials, such as inorganic sulfuric acid and organic phthalic anhydride. The catalytic oxidation performance of V_2O_5 is undoubtedly outstanding among many vanadium oxides in fine synthesis applications. Gopinath et al. reported that V_2O_5 directly catalyzed the conversion of aromatic aldehydes and alcohols to esters in the presence of hydrogen peroxide, and proposed an intermediate state of hemiacetals [1]. In subsequent explorations, acetals were used as substrates to be oxidized to methyl esters in methanol by V_2O_5 [2]. Singhal et al. have described the first observation for the oxidative cyanation of tertiary amines with sodium cyanide in presence of V_2O_5 using molecular oxygen as oxidant under mild reaction conditions [3]. Given these reports, one can justifiably look forward to developing an efficient and green catalytic oxidation system with V_2O_5.

Vanadium is a trace element in living organisms, especially marine life, which plays an important role in regulating the life appearance of animals, such as vanadium in insulin mimics [4]. After vanadium-containing haloperoxidases (V-HPO) were found in many marine organisms, the structure and catalytic performance were investigated, including the mechanism of V-HPO-catalyzed bromination [5], sulfoxidation, and cyclization of organic substrates, particularly, terpenes, indoles, and other biotransformations [6]. It was found that V_2O_5 nanowires surprisingly exhibited an intrinsic peroxidase-like activity that efficiently converts the classical peroxidase substrates such as 2,2-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) and 3,3,5,5,-tetramethylbenzdine in the presence of hydrogen peroxide [7]. The commercial V_2O_5 also showed bromoperoxidase - like performance at regioselective bromination of organic substrates by a halide anion. The selective monobromination of aromatic compounds by Mg-Al-layered double hydroxide- CO_3^{2-}-Br^- (LDH-CO_3^{2-}-Br^-) with V_2O_5 and hydrogen peroxide as the oxidant, with high para-selectivity, was reported [8]. Specific vanadium species, as catalytically active centers could perform like enzymes, but the catalytic mechanism has to date not been clarified. Attention has also been given to the biotransformation between terpenoids [9], so the effects of vanadium oxide species on them has also been investigated.

Forests emit large quantities of volatile organic compounds (VOCs), mainly terpenes [10], to the atmosphere. Their condensable oxidation products can form secondary organic aerosol, and contribute to the atmospheric particle burden with implications for air quality and climate [11]. Terpenes and terpenoids are one of the precious components of the biomass widely existing in pine tree and other plants [12], on which further exploration of fine utilization may well be justified, for improving the atmospheric environment. Per year, 250,000–300,000

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https://doi.org/10.1016/j.catcom.2020.106041
Received 24 February 2020; Received in revised form 6 May 2020

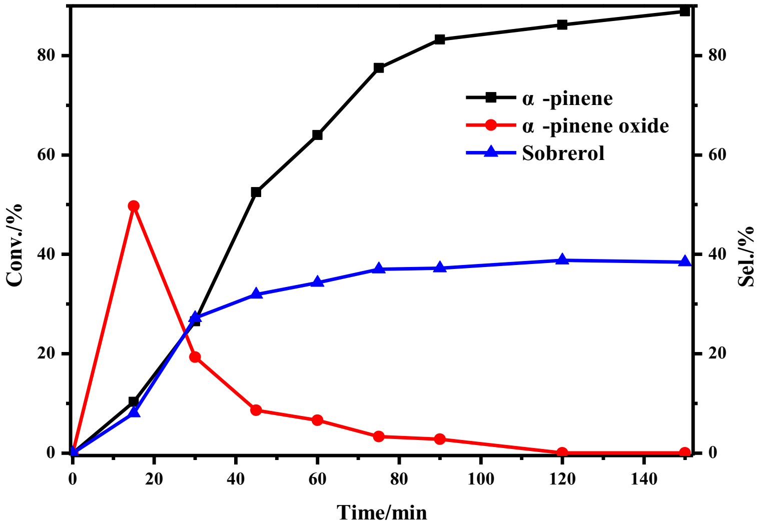


Fig. 1. Effect of time on oxidation of α-pinene by V_2O_5 with H_2O_2.

tons of turpentine are produced worldwide from wood pulp papermaking and resin tapping, from which about 100,000 tons are used for the production of terpenes and terpenoids for pharmaceutical, food, agricultural, and chemical industries that have developed them for their potentials and effectiveness as drugs, flavor enhancers, pesticides, and fine chemicals, respectively [13]. In particular, sobrerol, a monoterpenoid and well-known mucolytic agent (marketed as SOBREPIN), exhibited excellent physiological activity against obstructive respiratory diseases and has been widely investigated and applied [14]. In addition, it has certain application value in perfume, essential oils and other crude industries, and can also be used as an unsaturated monomer material for sustainable renewable polymers [15]. Sobrerol also has certain preventive and therapeutic effects on cardiovascular diseases which also play an important role in the treatment of *secret otitis media* in childhood [16,17]. Sobrerol was used as an adjuvant in combination with anesthetic drugs, inhibiting propofol metabolism to prolong anesthesia time [18]. It has even been reported in frontier research that sobrerol had demonstrated chemopreventive activity against mammary cancer at the initiation and development stages of carcinogen induction [19]. With the advancement of medical standards and detection means, sobrerol was found to be a novel and promising therapeutic agent for human colorectal cancer; it can restore the activity and efficacy of cetuximab in *ras* mutated tumors [20]. It is particularly desirable to develop higher value drugs as a combination treatment with sobrerol.

Hydrogen peroxide is a well-known green oxidant, which can efficiently promote olefin epoxidation in conjunction with transition-metal complexes [21] and, silicodecatungstate compounds [22], respectively. Kapoor et al. [23] discovered that titanium containing inorganic–organic hybrid mesoporous materials possessing catalytic activity in epoxidation of α-pinene using hydrogen peroxide, and recently another group presented a titanium-based silicalite epoxidation catalyst for the reaction [24]. Corina et al. [25] evaluated the catalytic performance of active vanadium nanospecies on MCM-41 for olefins in α-pinene oxidation with H_2O_2, in which α-pinene conversion only was 12.8%, and sobrerol selectivity was 36.0%; thus, direct investigation of V_2O_5-H_2O_2 for α-pinene oxidation is meaningful in academic knowledge and industrial application.

2. Experimental

V_2O_5 (0.15 mmol) was added to acetone (7 mL), and then an excess of H_2O_2 solution (30%, 20 mmol) was slowly added dropwise to obtain the vanadium solution at 293 K. α-Pinene (10 mmol) was added to the vanadium solution, and biomimetic hydroxylation reaction occurred. The products were analyzed using GC-2010 PLUSAF gas chromatography (Shimadzu, Japan) equipped with a capillary column and an FID detector. The GC mass balance was based on the substrate charged. The organic solvent was removed by rotary evaporation, and then the crude sobrerol separated out at room temperature. Sobrerol crystals were obtained by recrystallization from ethyl acetate, and its structure was determined by ^{1}H NMR, ^{13}C NMR, and 2D-NMR (HSQC). The representative GC spectra of crude reaction mixtures and the measured NMR spectra of sobrerol can be viewed in the Supporting Information.

3. Results and discussion

Although sobrerol can be isolated from the extracts of some plants (the content was 7 mg/kg from the fruits of *Illicium lanceolatum* [26]), there is also a documented chemical synthesis of sobrerol starting from methyl 3,5-dihydroxy-4-methyl benzoate in eight steps with an overall yield of 26% [27]. Alternatively, it can be prepared through converting α-pinene by microorganisms with biological enzymes, such as *Armillariella mellea*, which was incubated in 0.2% α-pinene for 4–5 days with a yield of sobrerol of 20% [28]. Generally, the raw materials for preparing sobrerol were mostly α-pinene oxide, which is an epoxidation product of α-pinene. First, α-pinene was oxidized to intermediate α-pinene oxide by peroxy organic acids, and then α-pinene oxide was converted to sobrerol through heating and hydration in an acidic medium.

Coincidentally, the vanadium content of *Armillariella mellea* was found to be around 0.2 mg/kg [29]. Vanadium was considered to be the component in the active center in the enzyme that converted α-pinene to sobrerol. Experiments were designed to verify this conjecture. α-Pinene oxide was generally considered an intermediate to sobrerol, which can be easily observed from Fig. 1. The effects of different peroxides on α-pinene oxidation with V_2O_5 were investigated, and the results are listed in Table S1. It is indicated that α-pinene was difficultly oxidized into sobrerol by other peroxides. This reaction process was split and then explored. Firstly, a peroxyacetic acid solution was prepared by acetic acid with 50% H_2O_2. Then, peroxyacetic acid solution efficiently oxidized α-pinene into α-pinene oxide below 15 °C with a yield of up to 85%. Finally, the conversion results of α-pinene and the intermediate product α-pinene oxide under different conditions were investigated. As shown in Table 1, α-pinene oxide was almost completely converted with the presence of acetic acid with a selectivity of sobrerol of 58.5%. In addition, V_2O_5 also can efficiently catalyze the conversion of α-pinene oxide to sobrerol in the presence of hydrogen peroxide which gave results similar to those of acetic acid. Therefore, in

Table 1

Conversion of α-pinene and α-pinene oxide by V_2O_5 with H_2O_2 in different media.

Entry	Mono-terpene	H_2O_2/ mmol	V_2O_5 /mmol	Add.	Conv. /%	Sel.[b] /%
1	α-pinene	20	0.15	None	89.7	49.0
2		20	0.15	HAc	88.9	50.2
3		20	0.15	TEA	0	0
4	α-pinene	20	0.15	None	99.4	50.9
5	oxide	20	–	None	15.0	38.4
6[a]		–	0.15	None	0	0
7[a]		–	–	HAc	97.7	58.5

[a] Added the same amount of deionized water as hydrogen peroxide.

[b] For sobrerol.

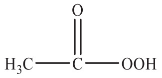
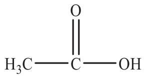
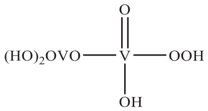
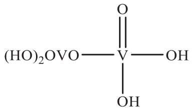
the process of dihydroxylation of α-pinene catalyzed by V_2O_5-H_2O_2, the addition of acetic acid had almost no effect on the formation of sobrerol, with a selectivity of 50.2%. However, with the introduction of the organic alkali triethanolamine, the reaction was difficult to achieve and the conversion of α-pinene was 0%. All the above experiments were performed at 20 °C.

XRD pattern and TEM spectrum of V_2O_5 were shown in Fig. S1, S2 respectively. It turned out to be the most common amorphous crystalline powder. V_2O_5-H_2O_2 catalytic system is recyclable, and the activity of vanadium does not change much. In this system, V_2O_5 was dissolved in H_2O_2 solution and the catalytic species was peroxo vanadium peracid in the system. Once finishing the reaction, V_2O_5 can be physically separated directly from the reaction system, with only a little vanadium remained in the aqueous solution which caused some mass loss of vanadium. The recycled V_2O_5 has similar catalytic activity for conversion of α-pinene to sobrerol as commercial V_2O_5.

Previously, various catalytic mechanisms of V_2O_5-H_2O_2 were proposed. Peroxovanadate can be formed and this provides a very notable, stable and excellent oxidation effect and was considered to be peroxidase-like active species [30]. The environment of the α-pinene transformation by V_2O_5-H_2O_2 was similar to the precursor solution of the V_2O_5-nH_2O_2 gel. So far, sol-gel syntheses of vanadium pentoxide gels have been grouped into three convenient routes [31]: (1) acidification of $NaVO_3$ using an ion-exchange process and polymerization of the resultant HVO_3 in water, (2) hydrolysis and condensation of vanadium alkoxide, and (3) reaction between H_2O_2 and amorphous V_2O_5. The formation of peroxovanadate occurred during the formation of V_2O_5-nH_2O_2 gel. Under acidic conditions, the formation of peroxovanadate was maintained in a solution with higher molar ratio of H_2O_2: V_2O_5. In situ ^{51}V NMR spectroscopy was used to monitor the formation process of vanadium gel [32] and it was found that vanadate oligomers were the main substance in the vanadium solution in the presence of an excess of H_2O_2. In these sol-gel syntheses routes, peroxovanadate was unstable and easily decomposed, showing high activity, but the monoperoxo cation had been observed to be a better oxidant than the diperoxo anion. The vanadate oligomers were oxidized by hydrogen peroxide, and then easily converted to peroxo vanadate peracid by hydrogen transfer [33]. The peroxo vanadate acid, $V^{V}O(OH)(OOH)$, in these processes was considered to have participated in the dihydroxylation of α-pinene. Density functional theory (DFT) calculations carried out using Gaussian 09 W, also provided sufficient and beneficial support for oligovanadate peracid. The B3LYP functional was employed and all calculations, including optimizations, frequencies and charge analysis, were performed using the 6–311 + G (d, p) basis set. All the atomic charges of their catalytically active centers were calculated employing the natural bond orbital (NBO) charge analysis and compared. The calculated atomic charges of the catalytically active species are listed in Table 2, showing values are close to the experimental reaction results.

Table 2

Atomic charges of active substances for oxidation of α-pinene by NBO analysis.

Entry	Molecule	-C**O**OH	-CO**O**H	-**O**H	-O**H**
1	 $H_3C-\overset{O}{\overset{\|}{C}}-OOH$	−0.326	−0.449		
2	 $H_3C-\overset{O}{\overset{\|}{C}}-OH$	–	–	−0.721	0.491
3	 $(HO)_2OVO-\underset{\underset{OH}{\vert}}{\overset{\overset{O}{\|}}{V}}-OOH$	−0.280	−0.442		
4	 $(HO)_2OVO-\underset{\underset{OH}{\vert}}{\overset{\overset{O}{\|}}{V}}-OH$	–	–	−0.717 −0.723	0.491 0.493

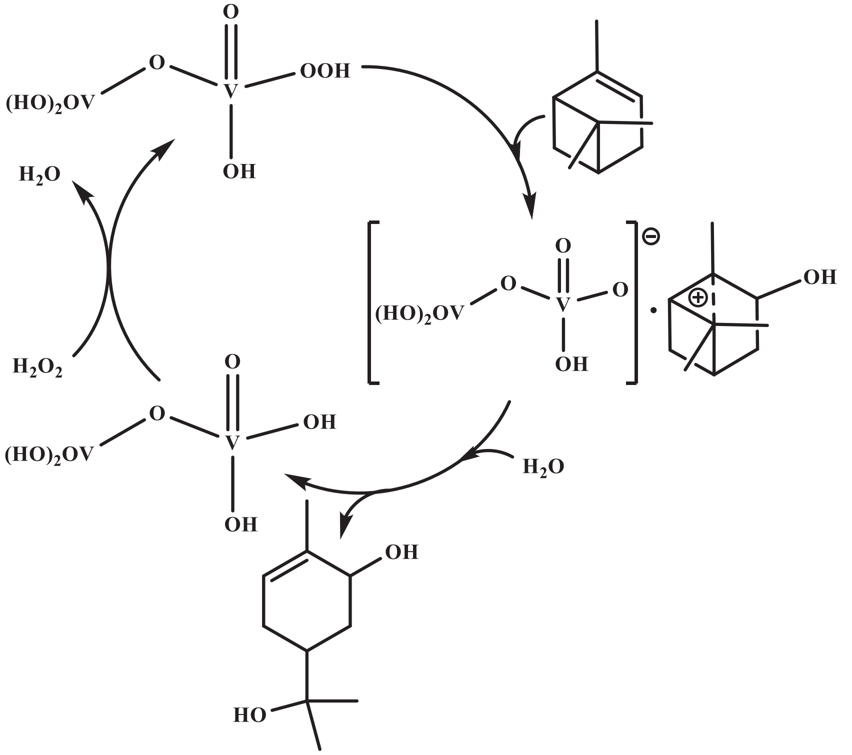
Conventionally, the conversion of α-pinene into sobrerol required two steps. In the first step, epoxidation of olefins was a very important oxygen transfer reaction, especially in commercial industry. There is no doubt that the peroxy species were the active group of this step, whether it was metal peroxo complex [34], organic peroxy compound, or inorganic peroxide. They behaved in the Lewis acid mechanism or the main element oxidation [35]. Similar mechanisms were considered to apply in the epoxidations of α-pinene by peracetic acid and such vanadium acid analogues. The oxygen atom, close to the hydrogen atom, of the peroxy group on peroxo vanadium acid oligomers and peroxyacetic acid had very similar charges and were both easily abstracted which conveniently promoted the electrophilic epoxidation of the olefin. The vanadic acid and acetic acid formed after oxygen transfer exhibited a similar intrinsic acid function and continued to promote the hydration reaction of the epoxide, as hydrogen atoms on their hydroxyl group had notably similar electronegativity, and it was dissociated to produce H^+ protons conveniently. Their similarities were confirmed by comparing the charge distribution values of the active species with values from the simulations (Table 2). Futhermore, we proposed the mechanism of dihydroxylation of α-pinene by V_2O_5-H_2O_2, as has been described by a catalytic cycle in Scheme 1. V_2O_5 was dissolved in a low concentration of hydrogen peroxide to obtain a vanadium (V) solution, which contained peroxo vanadium acid and vanadic acid. Peroxo vanadium acid transfered oxygen to α-pinene, and combined with it to form an ionic intermediate, followed by hydration to produce sobrerol. Vanadic acid was oxidized to peroxo vanadium acid in the presence of excess hydrogen peroxide.

4. Conclusions

In conclusion, peroxidase-like catalytic activity of commercial V_2O_5 in a mild environment with H_2O_2 was shown to have a better effect on the conversion of biomass pinene beyond the level of biotransformation with *Armillariella mellea*. The dihydroxylation of α-pinene by V_2O_5-H_2O_2 was an efficient and biomimetic green route to prepare sobrerol. The peroxo vanadium acid, $V^{V}O(OH)(OOH)$, was considered to be a source of catalytic species for the dihydroxylation of α-pinene to sobrerol.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



Scheme 1. Dihydroxylation of α-pinene by peroxo vanadium acid

Acknowledgements

The authors are grateful for the support extended to this work by the National Natural Science Foundation of China (No. 21776068, 21878074 and 21975070).

Appendix A. Supplementary data

XRD pattern and TEM spectrum of V_2O_5; representative GC spectra of crude product mixtures; ^{1}H NMR, ^{13}C NMR, and 2D-NMR (HSQC) spectra of sobrerol; experimental procedures for dihydroxylations of α-pinene; the contrast between peroxo vanadium peracid and peracetic acid in the epoxidation of α-pinene.

References

[1] R. Gopinath, B.K. Patel, A catalytic oxidative esterification of aldehydes using V2O5 − H2O2, Org. Lett. 2 (2000) 577–579.

[2] R. Gopinath, A. Paital, B. Patel, ChemInform Abstract: V2O5-H2O2: A Convenient Reagent for the Direct Oxidation of Acetals to Esters, ChemInform 33 (2010).

[3] S. Singhal, S.L. Jain, B. Sain, An efficient aerobic oxidative cyanation of tertiary amines with sodium cyanide using vanadium based systems as catalysts, Chem. Commun. (2009) 2371–2372.

[4] D. Sanna, G. Micera, E. Garribba, Interaction of insulin-enhancing vanadium compounds with human serum holo-transferrin, Inorg. Chem. 52 (2013) 11975–11985.

[5] J.N. Carter-Franklin, A. Butler, Vanadium bromoperoxidase-catalyzed biosynthesis of halogenated marine natural products, J. Am. Chem. Soc. 126 (2004) 15060–15066.

[6] A. Butler, M. Sandy, Mechanistic considerations of halogenating enzymes, Nature 460 (2009) 848–854.

[7] R. Andre, F. Natalio, M. Humanes, J. Leppin, K. Heinze, R. Wever, H.C. Schroder, W.E.G. Muller, W. Tremel, V2O5 nanowires with an intrinsic peroxidase-like activity, Adv. Funct. Mater. 21 (2011) 501–509.

[8] M. Ghiaci, M.E. Sedaghat, S. Ranjbari, A. Gil, Regioselective bromination of organic substrates by LDH-CO32 − −Br − promoted by V2O5–H2O2, Appl. Catal. A Gen. 384 (2010) 18–26.

[9] H.N. Bhatti, S.S. Khan, A. Khan, M. Rani, V.U. Ahmad, M.I. Choudhary, Biotransformation of monoterpenoids and their antimicrobial activities, Phytomedicine 21 (2014) 1597–1626.

[10] R.K. Pathak, C.O. Stanier, N.M. Donahue, S.N. Pandis, Ozonolysis of α-pinene at atmospherically relevant concentrations: Temperature dependence of aerosol mass fractions (yields), J. Geophys. Res.-Atmos. 112 (2007).

[11] M. Ehn, J.A. Thornton, E. Kleist, M. Sipila, H. Junninen, I. Pullinen, M. Springer, F. Rubach, R. Tillmann, B. Lee, F. Lopez-Hilfiker, S. Andres, I.H. Acir, M. Rissanen, T. Jokinen, S. Schobesberger, J. Kangasluoma, J. Kontkanen, T. Nieminen, T. Kurten, L.B. Nielsen, S. Jorgensen, H.G. Kjaergaard, M. Canagaratna, M. Dal Maso, T. Berndt, T. Petaja, A. Wahner, V.M. Kerminen, M. Kulmala, D.R. Worsnop, J. Wildt, T.F. Mentel, A large source of low-volatility secondary organic aerosol, Nature 506 (2014) 476.

[12] J.K. Muhlemann, A. Klempien, N. Dudareva, Floral volatiles: from biosynthesis to function, Plant Cell Environ. 37 (2014) 1936–1949.

[13] W. Schwab, C. Fuchs, F.-C. Huang, Transformation of terpenes into fine chemicals, Eur. J. Lipid Sci. Technol. 115 (2013) 3–8.

[14] A. Yuta, J.N. Baraniuk, Therapeutic approaches to mucus hypersecretion, Curr Allergy Asthma Rep 5 (2005) 243–251.

[15] M.S. Lima, C.S.M.F. Costa, J.F.J. Coelho, A.C. Fonseca, A.C. Serra, A simple strategy toward the substitution of styrene by sobrerol-based monomers in unsaturated polyester resins, Green Chem. 20 (2018) 4880–4890.

[16] L. Bellussi, D. Bernocchi, G. Ciferri, G. Manini, D. Passali, Sobrerol in the treatment of secretory otitis media in childhood, J. Int. Med. Res. 17 (1989) 277–286.

[17] C. Touvay, B. Vilain, C. Carre, J.M. Mencia-Huerta, P. Braquet, Effect of limonene and sobrerol on monocrotaline-induced lung alterations and pulmonary hypertension, Int. Arch. Allergy Immunol. 107 (1995) 272–274.

[18] A. Li Lin, N. Shangari, T.S. Chan, D. Remirez, P.J. O'Brien, Herbal monoterpene alcohols inhibit propofol metabolism and prolong anesthesia time, Life Sci. 79 (2006) 21–29.

[19] P.L. Crowell, Monoterpenes in breast cancer chemoprevention, Breast Cancer Res. Treat. 46 (1997) 191–197.

[20] S. Shapira, D. Kazanov, N. Arber, Monoterpenes: a novel and promising therapeutic agent, Found in Essential Oils, for Human Colorectal Cancer, Gastroenterology 150 (2016) S140.

[21] K.A. Joergensen, Transition-metal-catalyzed epoxidations, Chem. Rev. 89 (1989) 431–458.

[22] K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi, N. Mizuno, Efficient Epoxidation of olefins with ≥99% selectivity and use of hydrogen peroxide, Science 300 (2003) 964–966.

[23] M.P. Kapoor, A. Bhaumik, S. Inagaki, K. Kuraoka, T. Yazawa, Titanium containing inorganic–organic hybrid mesoporous materials with exceptional activity in epoxidation of alkenes using hydrogen peroxide, J. Mater. Chem. 12 (2002) 3078–3083.

[24] T. Zhang, L. Mazaud, L.-M. Chamoreau, C. Paris, A. Proust, G. Guillemot, Unveiling the active surface sites in heterogeneous titanium-based Silicalite Epoxidation catalysts: input of Silanol-functionalized Polyoxotungstates as soluble analogues, ACS Catal. 8 (2018) 2330–2342.

[25] C.M. Chanquía, A.L. Cánepa, E.L. Winkler, E. Rodríguez-Castellón, S.G. Casuscelli, G.A. Eimer, Nature of active vanadium nanospecies in MCM-41 type catalysts for olefins oxidation, Mater. Chem. Phys. 175 (2016) 172–179.

[26] J.F. Liu, H.J. Li, L.X. Wang, M.Q. Liu, Y.F. Bi, Y.B. Zhang, Two new monoterpenes from the fruits of Illicium lanceolatum, Molecules (Basel, Switzerland) 18 (2013)

11866–11872.

[27] Q. Wang, Y. Li, Q. Chen, A convenient, large scale synthesis of trans-(+)-Sobrerol, Synth. Commun. 33 (2003) 2125–2134.

[28] B. Draczyńska, C. Cagara, A. Siewiński, A. Rymkiewicz, A. Zabźa, A. Leufvèn, Biotransformation of pinenes XVII. Transformation of α-and β-pinenes by means of Armillariella mellea (honey fungus), a parasite of woodlands, J. Basic Microbiol. 25 (1985) 487–492.

[29] J. Vetter, Vanadium content of some common edible, wild mushroom species, Accred. Qual. Assur. 4 (1999) 39–48.

[30] H.B. ten Brink, H.L. Dekker, H.E. Schoemaker, R. Wever, Oxidation reactions catalyzed by vanadium chloroperoxidase from Curvularia inaequalis, J. Inorg. Biochem. 80 (2000) 91–98.

[31] H.X. Kai, M.D. Kun, L.J. Bo, X.S. Lin, L.J. Ying, Q.Y. Tai, V2O5·nH2O crystalline Nanosheets: hydrothermal fabrication and structure evolution, Chem. Lett. 36 (2007) 560–561.

[32] C.J. Fontenot, J.W. Wiench, M. Pruski, G.L. Schrader, Vanadia gel synthesis via Peroxovanadate precursors. 1. In situ laser Raman and 51V NMR characterization of the gelation process, J. Phys. Chem. B 104 (2000) 11622–11631.

[33] M.V. Kirillova, M.L. Kuznetsov, Y.N. Kozlov, L.S. Shul'pina, A. Kitaygorodskiy, A.J.L. Pombeiro, G.B. Shul'pin, Participation of Oligovanadates in alkane oxidation with H2O2 catalyzed by vanadate anion in acidified acetonitrile: kinetic and DFT studies, ACS Catal. 1 (2011) 1511–1520.

[34] G. Yin, Understanding the oxidative relationships of the metal Oxo, Hydroxo, and Hydroperoxide intermediates with manganese(IV) complexes having bridged Cyclams: correlation of the physicochemical properties with reactivity, Acc. Chem. Res. 46 (2013) 483–492.

[35] S.T. Oyama, Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis, Elsevier Science, 2011.