Selective Oxidation of Citronellol over Titanosilicate Catalysts

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Abstract: Citronellol is one of the most widely used fragrances for bouquetting purposes and it is a starting material for synthesis of several other terpenoids. Nevertheless, few data have been reported on citronellol selective oxidation. Accordingly, we report our findings on the selective oxidation of citronellol with hydrogen peroxide using a set of titanosilicate catalysts with different morphologies and textural properties—conventional titanium silicalite 1 (TS-1), mesoporous TS-1, layered TS-1 and silica-titania pillared TS-1 and also studying the effect of the solvent used. Epoxidation of C6=C7 double bond was the main primary reaction in this system and trace signals of C5 allylic oxidation products were observed without formation of citronellal. Due to the presence of post-synthesis introduced additional Ti sites, the silica-titania pillared TS-1 (TS-1-PiTi) provided the highest conversion among the tested catalysts; nevertheless, citronellol was oxidized over all the studied catalysts including conventional TS-1; therefore, showing that it penetrates even into MFI micropores (0.55 nm in diameter). When using acetonitrile as a solvent, the conversion was proportional to the titanium content of the catalyst. When studying the effect of the solvent, acetonitrile provided the highest epoxide selectivity (55%) while in methanol, 2-propanol and 1,4-dioxane, ring opening reactions caused epoxide decomposition.

Keywords: zeolite; titanosilicate; catalysis; oxidation; citronellol; epoxide; aldehyde

1. Introduction

Terpenes and terpenoids are important natural substances derived from isoprene (2-methylbuta-1,3-diene). Some of them are abundant and easily isolated from natural products, others are rare or difficult to isolate. They exhibit a high structural variability and typically contain a number of multiple bonds and oxygen functional groups. Terpenoids find their applications as fragrances or flavors as well as drug and other fine chemicals building blocks [1].

Selective oxidation is one of the important transformations of the terpenoids, leading to epoxides, polyols and other compounds of industrial importance. Particularly, these derivatives are reaction intermediates in several applications such as cosmetics, perfumes, food, dyestuffs, and pharmaceutical industries.

There exists a wide palette of heterogeneous selective oxidation catalysts including precious metals such as Pd, Ag, Au, and Pt [2,3]. Additionally, catalysts containing non-precious metals such as cobalt [4], titanium [5,6], molybdenum [7], nickel [8], silver and cerium [9], among others, can catalyze the oxidation of alcohols to aldehydes or ketones activating molecular oxygen for the selective oxidation. Of these, titanium provides particularly versatile catalysts. When used in the
form of TiO$_2$. Ti sites photo-activates molecular oxygen [10], while isolated titanium (IV) atoms, which are isomorphously incorporated in the framework of a zeolite, activate peroxides (including the particularly aqueous hydrogen peroxide) for a number of oxidation reactions including epoxidation, ammoxidation, phenol hydroxylation and alcohol oxidation [11].

Zeolites are originally microporous crystalline aluminosilicates. Other elements such as B, Fe, Ge, Ga and Ti can be incorporated instead of aluminum; thus, tuning the acidity and obtaining redox properties [12]. Due to their high thermal and mechanical stability, structure uniformity and the avoidance of using heavy or precious metals, zeolite catalysts meet current demands of green chemistry [13].

Titanium silicalite 1 (TS-1, MFI structure) is the first reported titanosilicate zeolite [14], and it remains one of the most studied titanosilicates due to its industrial relevance as well as recent advances in making its hierarchical [15] and layered forms [6,13]. The hierarchical and layered forms of TS-1 are particularly important in selective oxidation of large molecules such as terpenoids since they overcome diffusion and shape restrictions posed by conventional microporous TS-1. In other words, hierarchical TS-1 (possessing transport mesopores in addition to micropores) or layered TS-1 [16] (having one of the crystal dimensions reduced to a unit cell level and thus possessing high external surface) enables sterically demanding branched and cyclic molecules to reach active sites, which are inaccessible in conventional TS-1 because they can be reached only through the narrow microporous channel system.

Citronellol (3,7-dimethyloct-6-en-1-ol) is one of the most widely used fragrances and it is used for bouquetting purposes in citrus flavor compositions. Citronellol is isolated from natural sources (e.g., geranium oil, rose oil) and it is a starting material for making 7-hydroxydihydrocitronellal by a two-step hydration selective oxidation procedure [17]. Nevertheless, very few data have been reported on citronellol selective oxidation using a titanosilicate catalyst. The only report mentions formation of 7-methoxy-3,7-dimethylocta-1,6-diol as a main product (selectivity 86% at 64% conversion) over Ti-Al-beta catalyst (a large pore titanosilicate zeolite possessing strongly acidic aluminum sites) with hydrogen peroxide as an oxidant in methanol [18]. This result suggests a preferential epoxidation of C=C double bond over oxidation of the –OH group to an aldehyde; however, product distribution as well as other aspects influencing the reaction (catalyst morphology, solvent effect) when using aluminum-free titanosilicate catalysts remains to be disclosed.

In the present contribution, we report on our findings on selective oxidation of citronellol with hydrogen peroxide using a set of hierarchical and layered TS-1 catalysts. More specifically, a structure–activity relationship was studied on a set of catalysts with different morphologies and textural properties—conventional TS-1 zeolite, mesoporous TS-1, layered TS-1 [16] and silica-titania pillared TS-1 [19]. In addition, the solvent effect was investigated, testing methanol, acetonitrile, 2-propanol and 1,4-dioxane.

2. Results and Discussion

2.1. Catalyst Characterization

The aluminum-free titanosilicate catalyzed citronellol oxidation with hydrogen peroxide was investigated using a set of TS-1 catalysts with different morphologies. The conventional TS-1 (TS-1-Z) is a conventional TS-1 industrial reference catalyst. Mesoporous TS-1 (meso-TS-1) is a hierarchical catalyst prepared by hard templating with carbon nanoparticles of 20 nm size. These nanoparticles were incorporated into the TS-1 crystals and when the catalyst was calcined, a system of mesopores remained in place of the hard template particles. Layered TS-1 (lam-TS-1) was synthesized using a special surfactant template developed by the Ryoo group [16]. It consists of single crystals with the dimension along the $b$-crystallographic axis reduced to a unit cell thickness. Silica-titania pillared TS-1 (TS-1-PITi) is a silica-titania pillared catalyst prepared from lam-TS-1. When calcining lam-TS-1, the distance between individual crystals decreases because these are originally supported by the surfactant template, which is removed. Pillaring helps to preserve the interlayer distance because the
amorphous silica pillars support the layers even after surfactant removal. The addition of a titanium source during pillaring compensates the material active phase dilution [19]. Table 1 lists all the catalysts, their titanium content and textural properties. Particularly note the strongly increased external surface area of the layered lam-TS-1 and TS-1-PITi catalysts in comparison with the conventional TS-1-Z and hierarchical meso-TS-1.

Table 1. Titanium content and textural properties of the catalysts used in the study.

| Catalyst   | Morphology      | Si/Ti (mol/mol) | $S_{BET}$ (m$^2$/g) | $V_{mic}$ (cm$^3$/g) | $V_{tot}$ (cm$^3$/g) | $S_{ext}$ (m$^2$/g) |
|------------|-----------------|-----------------|---------------------|----------------------|----------------------|---------------------|
| TS-1-Z     | Conventional    | 28              | 510                 | 0.10                 | 0.28                 | 31                  |
| Meso-TS-1  | Hierarchical    | 43              | 432                 | 0.09                 | 0.31                 | 29                  |
| Lam-TS-1   | Layered         | 49              | 440                 | 0.09                 | 0.34                 | 238                 |
| TS-1-PITi  | Layered-pillared | 22              | 580                 | 0.09                 | 0.35                 | 369                 |

Crystalline structure of the prepared catalysts was characterized by XRD analysis (Figure 1). TS-1-Z and meso-TS-1 exhibit a sharp XRD pattern consistent with MFI zeolite crystalline structure. No additional crystalline phases were observed. The XRD patterns of lam-TS-1 and TS-1-PITi are less sharp, which is a result of missing long range order along the crystallographic $b$-axis, and it is fully consistent with data reported for this type of material [16,20]. Shoulder approximately $2\theta = 1.5^\circ$ reflects interlayer spacing of both layer-containing samples being more intensive for the TS-1-PITi, where the layers are supported by the amorphous pillars.

Isomorphous incorporation of the Ti atoms in the zeolite structure is the key to the catalytic activity of titanosilicate zeolites. Presence of Ti in the framework positions with tetrahedral coordination is evidenced by a fingerprint band at 960 cm$^{-1}$ in the infra-red (IR) (Figure 2) spectrum of the catalyst [21] and by a characteristic UV–VIS band (Figure 3) centered at 210 nm [21]. The IR fingerprint band can be identified in the spectra of all catalysts. The UV–VIS spectra also confirm the presence of tetrahedrally coordinated titanium. Additional adsorption bands in the spectrum of TS-1-PITi in the region of
approximately 240–290 nm reflect the presence of isolated titanium species with coordination number 5–6 attached to the framework, which were created by the post-synthesis titanium addition during pillaring [19]. On the other hand, absence of absorption bands above 300 nm (except meso-TS-1) proves absence of the TiO$_2$ anatase-like phase, which is catalytically inactive.

![Figure 2. FTIR spectra of TS-1-Z (black), meso-TS-1 (red), lam-TS-1 (blue) and TS-1-PITi (green).](image-url)

![Figure 3. Diffuse reflectance UV–VIS spectra of TS-1-Z (black), meso-TS-1 (red), lam-TS-1 (blue) and TS-1-PITi (green).](image-url)
We conclude that the characterization data of all the prepared catalysts are consistent with literature originally reporting their preparation and the catalysts are of a sufficient quality to assess their performance in catalysis of citronellol selective oxidation.

2.2. Selective Catalytic Oxidation of Citronellol

Citronellol was selectively oxidized with aqueous hydrogen peroxide using the above described titanosilicate catalysts with different morphologies and textural properties. In addition, the solvent effect on the reaction was investigated by testing the reaction in methanol, acetonitrile, 2-propanol and 1,4-dioxane. Methanol is a typical solvent of choice when epoxidizing small substrates over TS-1 catalysts [6]. However, in some cases (including citronellol, see below), methanol reacts with the epoxides formed in acid catalyzed ring opening reactions. In contrast, acetonitrile does not react with epoxides and in addition it suppresses any acid catalyzed reactions due to its basic character. Therefore, it is the second most frequently used solvent for oxidation reactions over titanosilicates [22,23].

In addition, bulkier 2-propanol, which can also react with epoxides forming 2-propyl hydroxy ethers, was selected, and 1,4 dioxane was used as a solvent, which is inert both to epoxides and acid sites.

Citronellol is a branched hydrocarbon with one C=C double bond and one primary hydroxyl group. Therefore, it has three possible primary oxidation products (Scheme 1): citronellol epoxide (3,7-dimethyl-6,7-epoxyoctan-1-ol) being a product of C6=C7 bond epoxidation; citronellal (3,7-dimethyl-6-oct-1-en-1-al) being a product of the hydroxyl group oxidation; and 3,7-dimethyl-6-en-1,5-diol being a product of C5 allylic oxidation. These primary products can undergo various subsequent reactions. Of these, the most significant is acid catalyzed epoxide ring opening reaction with water or alcohol solvent (particularly methanol).

Figure 4 presents citronellol conversion curves and epoxide selectivity curves in acetonitrile and methanol. TS-1-PITi provided the highest conversion of the tested catalysts in both solvents. The trend among the rest of the catalysts is different in acetonitrile and methanol, showing that citronellol penetrates even through TS-1 micropores.

The conversion trend in acetonitrile (conversion after 180 min: TS-1-PITi 30% > TS-1-Z 22% > mesoTS-1 19% > lam-TS-1 17%) increases linearly with the titanium content (Table 1) and it does not follow any of the textural properties; therefore, supporting the above hypothesis that citronellol enters even TS-1 micropores. Citronellol epoxide was the main observed product in all the reactions reaching 71% selectivity over TS-1-Z and 68% selectivity over meso-TS-1 in citronellol conversion range 0–30%. Selectivities over lam-TS-1 (55%) and TS-1-PITi (40%) were lower in the same conversion range. Based on our results reported for linalool, norbornene and cyclooctene [24], we speculate that the catalyst hydrophobicity is the selectivity driving parameter in the case of citronellol, since the selectivity follows the expected hydrophilicity trend (conventional TS-1 and meso-TS-1 bearing less terminal silanol groups and thus being less hydrophilic than lam-TS-1 and TS-1-PITi). The more hydrophilic catalysts support the epoxide ring opening reaction with water. Products of C5 allylic oxidation (3,7-dimethyl-6-en-1,5-diol and 3,7-dimethyl-6-en-1-ol-5-one) were identified as side products over the lam-TS-1 and TS-1-PITi. The signals of the C5 allylic oxidation products were more intense over the TS-1-PITi than over lam-TS-1. Formation of citronellal was not observed except a trace amount in the reaction over TS-1-PITi.

The selective oxidation in methanol (Figure 4c,d) occurred in a different way. TS-1-PITi provided the highest conversion (i.e., 28.5% after 120 min) while the other catalysts did not differ significantly, providing conversions of 12% (lam-TS-1) and 10% (TS-1-Z, meso-TS-1) after the same reaction time. This observation suggests that the active sites that were introduced post-synthesis into the TS-1-PITi may be significantly more active in methanol than those formed during hydrothermal synthesis, most likely because of their location on the external surface of the catalyst. Citronellol epoxide was the main product only when using lam-TS-1 as catalyst (selectivity 47% up to 20% conversion), in all the other reactions, 3,7-dimethyl-7-methoxyoctan-1,6-diol, an epoxide ring opening product with methanol, was the main product (evidenced, i.a., by an ion m/z = 73 (CH₃(CH₃-O)-C⁺-CH₃ in the
Formation of this product is also in accordance with elder data obtained using the TiAl-beta catalyst [18]. In the reaction over TS-1-PITi, no epoxide was observed while when using TS-1-Z and meso-TS-1, the epoxide yield as a function of conversion went through a maximum below 10% conversion and then dropped to zero during the course of the reaction. The reason why this did not happen over lam-TS-1 is unclear. In addition, minor amounts of C5 allylic oxidation products (see above) were observed but not quantified.

**Scheme 1.** Citronellol selective oxidation pathways: epoxidation, –OH group oxidation, and allylic oxidation. Note, * 3,7-dimethylocta-1,6,7-triol was not observed in the gas chromatography (GC) due to its high boiling point but its formation is highly expectable.

Lam-TS-1 was used as a representative catalyst to investigate the solvent effect by also testing in 2-propanol and 1,4-dioxane (Table 2). Use of these solvents did not bring any significant improvement. Conversion after 180 min of the reaction was lower in 2-propanol (11.4%) and in 1,4-dioxane (9.9%) than in methanol (15.1%) and in acetonitrile (16.6%). We assume this is mainly due to the increased size of the solvent molecules. The solvent diffuses through catalyst channels together with the reactants and therefore slower diffusion of more bulky solvent molecules can also slow down the diffusion...
of the reactants. At the same time, lower epoxide selectivities (2-propanol: 36% and 1,4-dioxane: 31%) were observed in comparison with acetonitrile (55%) and methanol (47%). We ascribe the decrease in the selectivity to the lack of basic properties of acetonitrile in combination with lower polarity, which may support water adsorption on the hydrophilic surface of the lam-TS-1 catalyst and subsequently the ring-opening reactions with water.

TS-1-PITi). The more hydrophilic catalysts support the epoxide ring opening reaction with water. Products of C5 allylic oxidation (3,7-dimethyloct-6-en-1,5-diol and 3,7-dimethyloct-6-en-1-ol-5-one) were identified as side products over the lam-TS-1 and TS-1-PITi. The signals of the C5 allylic oxidation products were more intense over the TS-1-PITi than over lam-TS-1. Formation of citronellal was not observed except a trace amount in the reaction over TS-1-PITi.

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Figure 4. Conversion curves (top) and conversion vs. epoxide yield (selectivity) plot (bottom) for epoxidation of citronellol over TS-1-Z (black), meso-TS-1 (red), lam-TS-1 (blue) and TS-1-PITi (green) in acetonitrile (a,b) and in methanol (c,d) at 60 °C; numbers inside bottom figures give epoxide selectivity as a slope of the conversion vs. epoxide yield plot.

Table 2. Citronellol conversion and epoxide yield after 180 min of the reaction over lam-TS-1 catalyst at 60 °C in different solvents; selectivity to the epoxide is evaluated in conversion range 5–20% as a slope of conversion vs. yield dependence.

| Solvent     | Conversion (%) | Epox. Yield (%) | Selectivity (%) |
|-------------|---------------|-----------------|-----------------|
| Methanol    | 15.1          | 7.2             | 47              |
| 2-propanol  | 11.4          | 4.0             | 36              |
| 1,4-dioxane | 9.9           | 2.1             | 31              |
| Acetonitrile| 16.6          | 9.1             | 55              |

Notably, citronellol epoxide and products of its decomposition were the main products observed in our catalytic test while we observed only traces of citronellal when using TS-1-PITi catalyst. Tatsumi et al. [25] studied competitive oxidation of C=C double bond and –OH group over TS-1 and SiO2-TiO2 mixed oxide catalysts oxidizing a group of C3–C5 unsaturated alcohols showing that selectivity between epoxide and aldehyde depends i.a. on C=C bond substitution and –OH group
position in the molecule. Epoxidation was always the preferred reaction when using the TS-1 catalyst except in a case when the C=C bond was hindered by a methyl substituent. In contrast, we observed exclusive –OH group oxidation when oxidizing verbenol using i.a. both layered TS-1 and TS-1-PITi similar to those used in the present study [19]; however, verbenol is a substrate where the C=C bond is strongly strained and sterically hindered by a methyl groups on a C1–C5 bridge.

We also tested oxidation of benzyl alcohol and epoxidation of 2-hexene over the lam-TS-1 at 60 °C. Benzyl alcohol was selectively oxidized to benvaldehyde; however, the reaction was rather slow, reaching 3% conversion after 5 h and 5.2% after 24 h. Furthermore, 2-hexene, a small linear molecule, was oxidized rapidly (Figure 5) reaching a conversion of 40% after 4 h, when the reaction did not proceed further probably due to runout of the oxidant. Epoxide selectivity was 32% at this conversion, which is rather low in comparison with results reported by Kubota and Inagaki (epoxide selectivity 95%, o-xylene (99%), mesitylene (99%), 2-hexene (97%, mixture of isomers) and hydrogen peroxide 40% (>99%), 2-propanol (99%), 1,4-dioxane (99%), benzyl alcohol (99.5%), benzaldehyde (60% conversion using TS-1 catalyst) [26]. We assume this results from the combination of a lam-TS-1 catalyst and methanol solvent, which does not suppress ring opening reactions and it is in accordance with previous conclusions that a specific substrate requires a catalyst with a tailored pore system. In other words, conventional TS-1 provides higher conversion and selectivity than its more open forms (e.g., lam-TS-1) when oxidizing small linear olefins [6].

![Figure 5. Conversion curve of 2-hexene epoxidation over lam-TS-1 in methanol at 60 °C.](image)

3. Materials and Methods

3.1. Materials

Silicon (IV) ethoxide (TEOS; 98%), titanium (IV) butoxide (TBOT; 97%), methanol (99%), acetonitrile (99%), 2-propanol (99%), 1,4-dioxane (99%), benzyl alcohol (99.5%), benzaldehyde (>99%), β-citronellol (95%), α-xylene (99%), mesitylene (99%), 2-hexene (97%, mixture of isomers) and hydrogen peroxide 40% (w/w) were all purchased from Sigma-Aldrich (now Merck KGaA, Darmstadt, Germany). Surfactant template C_{18}H_{37}N+(CH_{3})_{2}C_{6}H_{12}N+(CH_{3})_{2}C_{6}H_{13} in the hydroxide form (C_{18-6-6}OH_{2}) was prepared as described in the literature [16]. Hard template carbon black pearls (particle size 20 nm) were purchased from Cabot Corp., Boston, MA, USA.

3.2. Catalyst Preparation

Conventional TS-1 (TS-1-Z) was kindly provided by Zeolyst International, Delfizjil, The Netherlands.
3.2.1. Mesoporous TS-1

The mesoporous TS-1 (meso-TS-1) was prepared using carbon black pearls (CBP, particle size 20 nm) as a hard template [27]. Then, 6 g of CBP was activated at 120 °C for 24 h. Next, 0.59 g of TBOT and 15.28 g of TEOS (corresponding to molar Si/Ti ratio 43) were mixed in a beaker and stirred for 20 min. Then, 42.98 g of distilled water was added slowly under vigorous stirring, followed by 9.32 g of tetrapropylammonium hydroxide (TPAOH) aqueous solution (40% wt.). The mixture was further stirred for 1 h and then activated CBP were introduced in portions. Finally, the thick black synthesis gel was stirred manually with a spatula for about 15 min. The resulting mixture with a molar composition of 100 TEOS: 2.32 TBOT: 25 TPAOH: 4000 H$_2$O: 670 C was divided into 4 Teflon-lined autoclaves (volume 100 mL each) and left to crystallize under hydrothermal conditions and agitation (60 rpm) at 175 °C for 60 h. Crude meso-TS-1 was filtered off, washed with copious amounts of water, dried at 60 °C for 24 h and finally calcined in an air stream (10 Nl/h) at 550 °C for 8 h with a temperature ramp of 2 °C/min.

3.2.2. Layered TS-1

The synthesis of layered TS-1 (lam-TS-1) was carried out according to a procedure reported in ref. [16]. First, 2.722 g of TBOT was added dropwise into 83.46 g of TEOS and stirred for 30 min. Then, an aqueous solution of the template C$_{18}$-6-6 OH$_2$ (0.028 mL in 404 g of distilled water) was added to the mixture. The synthesis mixture was heated and homogenized at 60 °C for 3 h. Evaporated ethanol was replaced with the same mass amount of water (100 mL of water was added after this time). The final synthesis mixture with a molar composition of 100 TEOS: 2.5 TBOT: 6 C$_{18}$-6-6 OH$_2$: 5600 H$_2$O was hydrothermally crystallized in a stainless steel autoclave (volume 1000 mL) with a stirring turbine (stirring speed 200 rpm) at 155 °C for 400 h. After the given time, the zeolite was filtered off, washed with copious amounts of water, and dried at 60 °C. Part of the product was calcined to yield lam-TS-1; part was subjected to a pillaring treatment, being the parent for TS-1-PITi. Calcination was carried out in an air stream (10 Nl/h) at 570 °C for 8 h, using a temperature ramp of 1 °C/min.

3.2.3. Silica-Titania Pillared TS-1

The silica-titania pillared TS-1 (TS-1-PITi) was prepared using our procedure reported earlier in ref. [19]. A mixture of TEOS and TBOT in a molar Si/Ti ratio 30 was mixed with the above described non-calcined dry lam-TS-1 (10 g of the pillaring mixture per 1 g of the zeolite) and stirred at 65 °C for 24 h. After the given time, the mixture was centrifuged, the liquid part was removed, and the solid material was dried for 48 h at room temperature. Subsequently, the solid product was hydrolyzed in water containing 5% vol. of ethanol (100 mL of water/1 g of zeolite) at ambient temperature for 24 h under vigorous stirring. Finally, the solid material was filtered, dried at 65 °C and calcined in an air stream (10 Nl/h) at 550 °C for 10 h with a temperature ramp of 2 °C/min.

3.3. Instrumentation

X-ray powder diffraction (XRD) patterns were collected using a Bruker (Billerica, MA, USA) D8 Advance diffractometer using CuKα radiation in Bragg–Brentano geometry with an energy-dispersive LynxEye XE-T detector using Cu Kα1 radiation. Data were collected in continuous mode.

Textural properties were evaluated from nitrogen adsorption/desorption isotherms at −196 °C, which were collected using a Micromeritics (Norcross, GA, USA) Triflex instrument. The BET area was evaluated from adsorption data at the relative pressure from $p/p_0 = 0.05$ to $p/p_0 = 0.2$. The t-plot method was applied to estimate external surface area ($S_{ext}$) and micropore volume ($V_{mic}$). The adsorbed amount at $p/p_0 = 0.97$ was used to calculate the total pore volume ($V_{tot}$).
Fourier transformation infrared spectra (FTIR) were collected using attenuated total reflection (ATR) technique on a Thermo Fischer Scientific (Waltham, MA, USA) Nicolet iS50 spectrometer with a transmission MTC/B detector at room temperature.

Elemental composition of the samples was determined by the Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) technique after dissolving the samples in HF.

Diffuse reflectance UV–VIS spectra were collected on an Agilent Technologies (Santa Clara, CA, USA) Cary 4000 UV–VIS spectrophotometer. Spectra intensity was evaluated in terms of the Kubelka–Munk function.

Samples from catalytic experiments were analyzed using a gas chromatography (GC) instrument (GC 7890A, Agilent Technologies, Santa Clara, CA, USA) equipped with a flame ionization detector (FID) and an Agilent HP-5 30 m × 0.32 mm × 0.25 µm column.

Gas chromatography-mass spectrometry (GC-MS) analyses were performed using a Thermo Fischer Scientific (Waltham, MA, USA) system consisting of a Trace 1310 GC and an ISQ LT single quadrupole mass spectrometer. MS spectra were collected in an m/z range 40–400 using standard electron impact ionization with electron energy of 70 eV.

3.4. Catalytic Experiments

Citronellol epoxidation experiments were carried out in a 25 mL round bottom flask heated by an aluminum block and equipped with a magnetic stirrer and reflux condenser at 60 °C. Typically, 9 mL of solvent was mixed with 60 mg of an activated catalyst (activation at 450 °C for 90 min and subsequent cooling in a desiccator), 250 µL of internal standard (mesitylene) and 1097 µL (6 mmol) of citronellol. The reaction mixture was heated to the reaction temperature, a zero sample was taken, and the reaction was started at $t = 0$ min by addition of 613 µL of 30% H$_2$O$_2$ aqueous solution (corresponding to 6 mmol of H$_2$O$_2$). Samples of the reaction mixture were taken in regular intervals, the catalyst was immediately removed by centrifugation and samples were analyzed by GC analysis. Products were identified by comparison of the chromatogram retention times with standards where available (benzaldehyde, citronellal, or using GC-MS analysis of the samples). GC-MS spectra were interpreted combining comparison of the obtained spectra with a U.S. National Institute of Standards and Technology (NIST) library and molecular fragment analysis.

Oxidations of benzyl alcohol and 2-hexene were carried out using the same experimental setup. The reaction mixture consisted of 5 mL of methanol, 50 mg of an activated catalyst, 200 µL of o-xylene as an internal standard, and 2.5 mmol of benzyl alcohol or 2-hexene—the reaction was initiated by addition of 213 mg of 40% H$_2$O$_2$ aqueous solution (2.5 mmol of H$_2$O$_2$).

4. Conclusions

We investigated selective oxidation of citronellol over conventional TS-1, mesoporous TS-1, layered TS-1 and silica-titania pillared TS-1 in different solvents using aqueous hydrogen peroxide as the oxidant. The catalysts differ in textural properties and TS-1-PITi also contains post-synthesis added titanium sites on the external surface. The TS-1-PITi was the catalyst that provided the highest conversion due to the presence of these additional sites, which are also well accessible; nevertheless, citronellol was oxidized over all the catalysts in the study, including conventional TS-1. In acetonitrile, the citronellol conversion was found to be proportional to the catalyst titanium content, unlike other, more sterically demanding, substrates [24].

Epoxidation of C6=C7 double bond of citronellol was the preferred oxidation pathway in all cases. The product distribution and reaction selectivity were strongly influenced by the solvent choice. In methanol, the epoxidation was followed by a ring opening reaction with the solvent, which did not occur in acetonitrile. Furthermore, 2-propanol and 1,4-dioxane provided even lower selectivity to the epoxide due to their lower polarity (expected to result in increased water adsorption on the catalyst surface) and lack of basic properties, which prevent ring opening reactions while using acetonitrile. Oxidation of the –OH group forming citronellal was not favored in any of the solvents.
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References
1. Sell, C.S. Fundamentals of Fragrance Chemistry; Wiley-VCH: Weinheim, Germany, 2019.
2. Davis, S.E.; Ide, M.S.; Davis, R.J. Selective oxidation of alcohols and aldehydes over supported metal nanoparticles. Green Chem. 2013, 15, 17–45. [CrossRef]
3. Mallat, T.; Baiker, A. Oxidation of alcohols with molecular oxygen on platinum metal catalysts in aqueous solutions. Catal. Today 1994, 19, 247–283. [CrossRef]
4. Murahashi, S.; Naota, T.; Hirai, N. Aerobic oxidation of alcohols with ruthenium-cobalt bimetallic catalyst in the presence of aldehydes. J. Org. Chem. 1993, 58, 7318–7319. [CrossRef]
5. Higashimoto, S.; Kitao, N.; Yoshida, N.; Sakura, T.; Azuma, M.; Ohue, H.; Sakata, Y. Selective photocatalytic oxidation of benzyl alcohol and its derivatives into corresponding aldehydes by molecular oxygen on titanium dioxide under visible light irradiation. J. Catal. 2009, 266, 279–285. [CrossRef]
6. Prech, J. Catalytic performance of advanced titanosilicate selective oxidation catalysts—a review. Catal. Rev. 2018, 60, 71–131. [CrossRef]
7. Velusamy, S.; Ahamed, M.; Punniyamurthy, T. Novel polyaniline-supported molybdenum-catalyzed aerobic oxidation of alcohols to aldehydes and ketones. Org. Lett. 2004, 6, 4821–4824. [CrossRef] [PubMed]
8. Choudary, B.M.; Kantam, M.L.; Rahman, A.; Reddy, C.V.; Rao, K.K. The First Example of Activation of Molecular Oxygen by Nickel in Ni-Al Hydrotalcite: A Novel Protocol for the Selective Oxidation of Alcohols. Angew. Chem. Int. Ed. Engl. 2001, 40, 763–766. [CrossRef]
9. Torbina, V.V.; Vodyankin, A.A.; Ten, S.; Mamontov, G.V.; Salaev, M.A.; Sobolev, V.I.; Vodyankina, O.V. Ag-based catalysts in heterogeneous selective oxidation of alcohols: A review. Catalysis 2018, 6, 447. [CrossRef]
10. Suib, S.L.; Prech, J.; Čejka, J.; Kuwahara, Y.; Mori, K.; Yamashita, H. Some novel porous materials for selective catalytic oxidations. Mater. Today 2020, 32, 244–259. [CrossRef]
11. Perez, C.; Carati, A.; Ingallina, P.; Mantegazza, M.A.; Bellussi, G. Production of titanium containing molecular sieves and their application in catalysis. Appl. Catal. A Gen. 2001, 221, 63–72. [CrossRef]
12. Mintova, S.; Barrier, N. Verified Synthesis of Zeolithic Materials, 3rd ed.; Elsevier (On behalf of Synthesis Commission of the International Zeolite Association): Amsterdam, The Netherlands, 2016.
13. Prech, J.; Pizarro, P.; Serrano, D.P.; Čejka, J. From 3D to 2D zeolite catalytic materials. Chemical Society Reviews. Chem. Soc. Rev. 2018, 47, 8263–8306. [CrossRef] [PubMed]
14. Taramasso, M.; Perego, G.; Notari, B. Preparation of Porous Crystalline Synthetic Material Comprised of Silicon and Titanium Oxides. U.S. Patent 4,410,501, 18 October 1983.
15. Perez-Ramirez, J.; Christensen, C.H.; Egeblad, K.; Christensen, C.H.; Groen, J.C. Hierarchical zeolites: Enhanced utilisation of microporous crystals in catalysis by advances in materials design. Chem. Soc. Rev. 2008, 37, 2530–2542. [CrossRef] [PubMed]
16. Na, K.; Jo, C.; Kun, J.; Ahn, W.S.; Ryoo, R. MFI Titanosilicate Nanosheets with Single-Unit-Cell Thickness as an Oxidation Catalyst Using Peroxides. ACS Catal. 2011, 1, 901–907. [CrossRef]
17. Surburg, H.; Panten, J. Common Fragrance and Flavor Materials: Preparation, Properties and Uses; Wiley-VCH: Weinheim, Germany, 2016.
18. Schofield, L.J.; Kerton, O.J.; McMorn, P.; Bethell, D.; Ellwood, S.; Hutchings, G.J. Oxidation of α-hydroxy containing monoterpenes using titanium silicate catalysts: Comments on regioselectivity and the role of acidity. J. Chem. Soc. Perkin Trans. 2 2002, 8, 1475–1481. [CrossRef]
19. Přech, J.; Eliášová, P.; Aldhayan, D.; Kubů, M. Epoxidation of bulky organic molecules over pillared titanosilicates. *Catal. Today* 2015, 243, 134–140. [CrossRef]

20. Choi, M.; Na, K.; Kim, J.; Sakamoto, Y.; Terasaki, O.; Ryoo, R. Stable single-unit-cell nanosheets of zeolite MFI as active and long-lived catalysts. *Nature* 2009, 461, 828. [CrossRef]

21. Ratnasamy, P.; Srinivas, D.; Knözinger, H. Active Sites and Reactive Intermediates in Titanium Silicate Molecular Sieves. *Adv. Catal.* 2004, 48, 1–169.

22. van der Waal, J.C.; Lin, P.; Rigutto, M.S.; van Bekkum, H. *Synthesis of Aluminium Free Titanium Silicate with the BEA Structure Using a New and Selective Template and Its Use as a Catalyst in Epoxidations*; Chon, S.-K.I.H., Sun, U.Y., Eds.; Elsevier: Amsterdam, The Netherlands, 1997; Volume 105, pp. 1093–1100.

23. van der Waal, J.C.; Rigutto, M.S.; van Bekkum, H. Zeolite titanium beta as a selective catalyst in the epoxidation of bulky alkenes. *Appl. Catal. A Gen.* 1998, 167, 331–342. [CrossRef]

24. Přech, J.; Kim, J.; Mazur, M.; Ryoo, R.; Čejka, J. Nanosponge TS-1: A Fully Crystalline Hierarchical Epoxidation Catalyst. *Adv. Mater. Interfaces* 2020, in press.

25. Tatsumi, T.; Yako, M.; Nakamura, M.; Yuhara, Y.; Tominaga, H. Effect of alkene structure on selectivity in the oxidation of unsaturated alcohols with titanium silicalite-1 catalyst. *J. Mol. Catal. A* 1993, 78, L41–L45. [CrossRef]

26. Kubota, Y.; Inagaki, S. High-Performance Catalysts with MSE-Type Zeolite Framework. *Top. Catal.* 2015, 58, 480–493. [CrossRef]

27. Wilde, N.; Přech, J.; Pelz, M.; Kubů, M.; Čejka, J.; Gläser, R. Accessibility enhancement of TS-1-based catalysts for improving the epoxidation of plant oil-derived substrates. *Catal. Sci. Technol.* 2016, 6, 7280–7288. [CrossRef]

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