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H_2O_2-based allylic oxidation of α-pinene over different single site catalysts

N.V. Maksimchuk [a], M.S. Melgunov [a], J. Mrowiec-Białoń [b], A.B. Jarzębski [b], O.A. Kholdeeva [a,*]

[a] *Boreskov Institute of Catalysis, Prospekt Akademika Lavrentieva 5, Novosibirsk, 630090, Russia*
[b] *Polish Academy of Sciences, Institute of Chemical Engineering, 44-100 Gliwice, Bałtycka 5, Poland*

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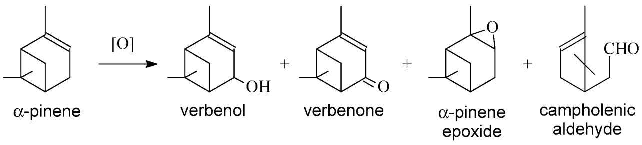
Abstract

Catalytic properties of different solids, containing Ti(IV), Zr(IV), and Fe(III) isolated in inorganic matrixes, have been assessed in allylic oxidation of α-pinene with aqueous H_2O_2. Among the catalysts studied were mesostructured metal silicates Ti-MMM-2 and Fe-MMM-2, TiO_2–SiO_2 mixed oxides, Ti and Zr grafted on mesoporous silica cellular foams (Ti- and Zr-MCF), and a new composite material, $H_5PW_{11}TiO_{40}$/silica, prepared by a sol–gel method. The catalysts were characterized by elemental analysis, N_2 adsorption, and DRS-UV. The Ti- and Zr-containing materials showed catalytic properties superior to those of Fe-MMM-2. The reaction selectivity strongly depended on the solvent properties, substrate/oxidant molar ratio, reaction temperature, and α-pinene conversion. In optimized reaction conditions (MeCN, 30 °C), the total selectivity toward verbenol/verbenone reached the maximal value of 80–82% at 8–15% conversion. The $H_5PW_{11}TiO_{40}$/silica catalyst can be used repeatedly without loss of activity and selectivity. No leaching of the active species occurs, and the oxidation is a true heterogeneous process operating via a radical nonchain mechanism.

Keywords: α-Pinene; Allylic oxidation; Verbenol; Verbenone; Ti(IV), Zr(IV), 'Single site' catalysts, mesoporous catalysts; Hydrogen peroxide

1. Introduction

α-Pinene is the main component of gum turpentine and thus is an inexpensive, readily available, and renewable starting material for producing a wide variety of valuable products, such as flavors, fragrances, medicines, and agrochemicals [1,2]. Specifically, its oxidation products (verbenol, verbenone, α-pinene epoxide, and campholenic aldehyde) are of high practical importance as flavor chemicals and key intermediates for the manufacture of various fine chemicals, including citral, menthol, taxol, and vitamins A and E [1–5]:



The development of catalytic methods for the selective α-pinene oxidation by "green" oxidants is a challenging goal of fine chemistry. Aqueous hydrogen peroxide can be the oxidant of choice because it is quite cheap, atom-efficient, and environmentally benign, and produces water as the only byproduct. Usually, H_2O_2-based oxidations require a catalyst to achieve an acceptable reaction rate and selectivity. The selective epoxidation of α-pinene with H_2O_2 can be performed using manganese [6–8], tungsten [9], and rhenium [10,11] catalysts in both homogeneous and heterogeneous forms.

With manganese (III) and (IV) complexes, the activity and selectivity were rather low [6,7]. Their heterogenization via anchoring to silica [8] or entrapping in zeolite [7] allowed improved selectivity; however, these catalysts were easily destroyed under the reaction conditions. The Venturello complex $[(C_8H_{17})_3NCH_3]_3PW_4O_{24}$ showed high selectivity in α-pinene epoxidation with H_2O_2 (92% selectivity at 83% α-pinene conversion) [9]. In the presence of CH_3ReO_3 as a homogeneous catalyst and an excess of pyridine, α-pinene epoxidation attained 90% selectivity at 100% conversion [10]. The polymer-supported CH_3ReO_3 catalyst was even more selective than

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[*] Corresponding author. Fax : +7-383-330-80-56.
E-mail addresses: nvmax@catalysis.nsk.su (N.V. Maksimchuk), khold@catalysis.nsk.su (O.A. Kholdeeva).

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the homogeneous one; the epoxide selectivity reached 100% at 98% conversion [11]. Alumina was used as a quite selective α-pinene epoxidation catalyst; however, anhydrous conditions should be used [12,13]. Mesoporous molecular sieves, Ti-MCM-41 and Ti-HMS, were reported to produce α-pinene epoxide with 100% selectivity at a low substrate conversion ($<6\%$) [14].

Although the achievable level of selectivity in α-pinene epoxidation is rather high, sufficient selectivity toward the allylic oxidation products, verbenol and verbenone, still remains a challenge. The autooxidation of α-pinene produces verbenol and verbenone with low yields [15–17]; cobalt compounds facilitate this reaction [18–29]. The maximal verbenol and verbenone selectivities (24 and 34%, respectively, at 40% substrate conversion) were reported for sol–gel Co/SiO_2 catalyst [29]. The allylic oxidation of α-pinene also proceeds smoothly with t-butyl hydroperoxide over copper salts [30] as well as with heterogeneous catalysts such as silica–titania co-gels [31], chromium aluminophosphate-5 [32], and Cr-pillared montmorillonite [33]. Moderate selectivity to verbenol and verbenone (41 and 12%, respectively, at 86% substrate conversion) were achieved using H_2O_2 in the presence of Pd(acac)$_2$ [30].

Molecular sieves and mixed oxides containing highly dispersed transition metal ions, so-called “single-site” catalysts, are well-known efficient catalysts for H_2O_2-based oxidation [34–64]. Unfortunately, many of these are not stable in the presence of aqueous H_2O_2 [47–49,53,58,59,61,65–67]. In this work, we assessed catalytic properties of different materials containing Ti(IV), Zr(IV), and Fe(III) ions isolated in inorganic matrixes, such as hydrothermally stable silicate MMM-2 [63], mesoporous cellular foam (MCF), and Keggin type heteropolytungstate, in allylic oxidation of α-pinene with H_2O_2. We paid special attention to study factors governing the reaction selectivity and to optimizing the reaction conditions. We evaluated the catalysts’ stability and recycleability.

2. Experimental

2.1. Materials

α-Pinene, containing 98% α-pinene and 2% β-pinene, was obtained by vacuum rectification of gum turpentine. Hydrogen peroxide was used as 30% in water, with its precise concentration determined iodometrically before use. Urea hydrogen peroxide adduct was purchased from Fluka. All other reactants were obtained commercially and used without further purification.

2.2. Catalyst preparation and characterization

The titanium-silicate, Ti-MMM-2, was prepared by hydrothermal synthesis under moderately acidic conditions using cetyltrimethyl ammonium bromide as a template according to a procedure described recently [63]. The iron-containing material, Fe-MMM-2, was synthesized following a similar procedure using $Na_2Si_2O_5$ and $FeCl_3$ as silica and iron sources [63]. Ti,Si-aerogel and xerogel were prepared as described previously [61]. Heteropolyacid $H_5PW_{11}TiO_{40}$ was synthesized following published methods [68]. The $H_5PW_{11}TiO_{40}$/silica composite material was prepared using tetramethoxysilane (TMOS) as the silica precursor via a two-step procedure similar to that described for the Co-polyoxometalate/silica material [69]. The molar ratio of reagents was as follows: Si:MeOH:H_2O:HCl = 1:9:6:0.0016. First, TMOS was prehydrolized using $1/2$ of the total amount of methanol, 0.2 M solution of HCl, and 2 mol of water per 1 mol of Si at 50 °C for 1 h. Then the solution containing the remaining half of the methanol, the rest of the water, and $H_5PW_{11}TiO_{40}$ (10 wt%) was added to the first solution under vigorous stirring. The gelation and aging (for 7 days) were performed at 50 °C. Wet gels were dried in vacuum at 60 °C for 6 h and then at 110 °C for 4 h. The pure silica sample was prepared by a similar procedure but without adding $H_5PW_{11}TiO_{40}$.

The structure of siliceous mesoporous cellular foams (MCF) was templated by oil in water microemulsions. The foams were prepared in an oil/water system composed of aqueous hydrochloric acid, the nonionic block copolymer surfactant Pluronic PE 9400 (BASF) and 1,3,5-trimethylbenzene. Tetraethoxysilane (TEOS) was used as a silica precursor. The preparation method was similar to that described previously [70]. In a typical procedure, Pluronic PE 9600 (0.4 mmol) was dissolved in 1.6 M HCl (75 mL) at room temperature. 1,3,5-Trimethylbenzene (17 mmol) and NH_4F (0.6 mmol) were added under vigorous stirring, and the mixture was heated to 60 °C. After 1 h of stirring, TEOS was added (4.4 g, 21.2 mmol). The mixture was further stirred for 2 h and subsequently stored at 60 °C for 20 h and at 100 °C for 24 h. After cooling to room temperature, the precipitate was separated by filtration, dried at room temperature for 4 days, and calcined at 500 °C for 8 h. Titanium and zirconium were introduced to MCF by a common postsynthesis grafting procedure [71]. Before grafting, the MCF samples were contacted with water vapor during 5 h and subsequently dried at 200 °C for 3 h. Titanium(IV) or zirconium(IV) isopropoxide dissolved in hexane were allowed to react with silanol groups present on the silica surface under reflux conditions for 24 h. Then hexane was removed by evaporation at 50 °C.

The textural characteristics of the catalysts were determined from nitrogen adsorption isotherms. The catalysts were also characterized by elemental analysis and DR-UV spectroscopy. To estimate catalyst stability, the samples were treated with aqueous 30% H_2O_2 (0.35 M) at 80 °C during 2 h in MeCN and then calcined at 500 °C for 1 h. To examine the hydrolytic stability of Ti-MCF, the samples were treated with water, MeCN–H_2O (1:1 v/v), MeCN–H_2O_2 (1:1 v/v), and 0.4 M H_2O_2 in MeCN for 2 h at 80 °C. Then each treatment sample was dried at 110 °C for 4 h.

2.3. Catalytic experiments

Catalytic experiments were carried out in thermostatic glass vessels under vigorous stirring at 25–80 °C. Typically, the reactions were initiated by adding 0.12 mmol of H_2O_2 to a mixture containing 0.1 mmol of α-pinene, 14 mg of a catalyst, an internal standard (biphenyl), and 1 mL of acetonitrile. Aliquots of reaction mixture were withdrawn periodically during the reaction course by syringe through a septum without opening the reactor. Each experiment was reproduced 2 or 3 times. The reaction products were identified by GC-MS and ^{1}H NMR, and quantified by GC. After the reactions, catalysts were filtered off, washed with methanol, dried in air at room temperature overnight and at 110 °C for 1–2 h, and then reused. The leaching tests were performed as described previously [58,59].

2.4. Instrumentation

GC analyses were performed using a Tsvet 500 gas chromatograph equipped with a flame ionization detector and a quartz capillary column (30 m × 0.25 mm) filled with Supelco MDN-5S. GC-MS analyses were conducted using an Agilent 6890 gas chromatograph (with a 30 m × 0.25 mm/HP-5 ms quartz capillary column) equipped with a quadrupole mass-selective detector (Agilent MSD 5973). DRS-UV measurements were performed on a Shimadsu UV–vis 2501PC spectrophotometer at ambient conditions. Nitrogen adsorption isotherms at 77 K were measured using both a Micromeritics ASAP 2000 instrument (Gliwice) and Quantachrome Autosorb-6BKr (Novosibirsk).

3. Results and discussion

3.1. Catalyst characterization

We previously reported the structural and textural properties of the hydrothermally stable Ti-MMM-2 material [63]. Briefly, this material has 2D hexagonally ordered mesopores with a narrow pore size distribution (mean diameter, 3 nm). The textural parameters of Ti- and Fe-MMM-2 used in this work are given in Table 1.

The pore size distributions calculated from both adsorption (cages) and desorption (windows) branches of N_2 isotherms at 77 K for Ti-MCF (Fig. 1) are narrow, in contrast to the broad distributions typically observed for aerogels [47,48,61]. To examine the hydrolytic stability of Ti-MCF, the sample was treated with several solutions, including water, MeCN–H_2O (1:1 v/v), MeCN–H_2O_2 (1:1 v/v), and 0.4 M H_2O_2 in MeCN (Table 2). Some decrease in the mesopore diameter and volume after treatment with pure water was seen, whereas no significant changes in porosity were observed after treatment with the H_2O_2–H_2O–MeCN solutions. This is in contrast to what we had observed earlier for the TiO_2–SiO_2 mixed oxides, the porous structure of which suffered from even small amounts of water introduced with H_2O_2 [61]. The moderate stability of the Ti-MCF porous structure makes this material a promising catalyst for H_2O_2-based oxidations.

To the best of our knowledge, the composite material $H_5PW_{11}TiO_{40}$/silica prepared by a sol–gel method has not yet been reported in the literature. According to the N_2 adsorption data, the $H_5PW_{11}TiO_{40}$/silica sample is nonporous (Table 1).

According to the general concept of single-site catalysts, the more isolated a metal ion is in an inert matrix, the higher its activity. It is well established that the absorption frequency in DR-UV spectra of titanium silicates depends on the coordination number of Ti(IV) and its dispersion in the silicate matrix [37–44]. A narrow band with a maximum at 211 nm observed in DR-UV spectra of Ti-MMM-2 (Fig. 2a) clearly signifies that titanium is presumably in a site-isolated, most likely tetrahedral-coordinated, form. For Ti-MCF, the UV absorption

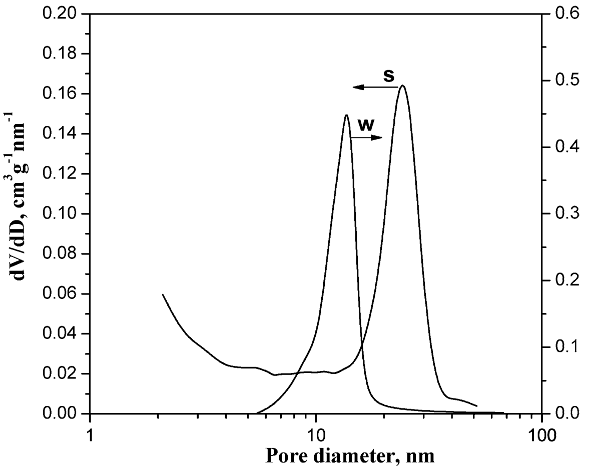

Fig. 1. Pore size distributions for cages (s) and connecting windows (w) in Ti-MCF after calcination determined from nitrogen adsorption and desorption isotherms.

Table 1
Physicochemical properties of the catalysts studied

Catalyst	Active metal[a] (wt%)	S_{BET} (m^2/g)	V_p[b] (cm^3/g)	d_p[c] (nm)	DRS-UV λ_{max} (nm)
$H_5PW_{11}TiO_{40}$/silica	0.15 (0.15)	<0.5	–	–	270 (216, 346, 434)[d]
Ti-MMM-2	1.8	1096	0.74	3.2	211
Ti-MCF	1.2 (1.2)	564	2.40	13	216
TiO_2–SiO_2-aerogel	3.5	695	2.20	12.4	236
TiO_2–SiO_2-xerogel	2.4	657	0.26	2.7	226
Zr-MCF	1.8	598	2.30	12.7	197 (240)[d]
Fe-MMM-2	1.8	925	0.48	3.2	221

[a] Weight percent of active metal in the sample (the wt% of Ti after three catalytic cycles of α-pinene oxidation inside parentheses; the reaction conditions are given in Table 3).

[b] Mesopore volume.

[c] Mesopore diameter.

[d] Shoulders in DR-UV spectra.

Table 2
Effect of different treatments on the textural properties of Ti-MCF

Treatment	S_{BET} (m^2/g)	V_p (cm^3/g)	d_p^{ads} (nm)	d_p^{des} (nm)
–[a]	541	2.34	23	13
–[b]	564	2.40	24	13
H_2O[c]	587	2.02	23	10
MeCN–H_2O (1:1 v/v)[c]	574	2.08	23	12.5
0.4 M H_2O_2 in MeCN[c]	588	2.34	24	13
MeCN–H_2O_2 (1:1 v/v)[c]	566	2.44	23	13

[a] After impregnation of MCF with Ti and drying at 110 °C for 4 h.

[b] After calcination (5 deg/min) for 2 h at 500 °C.

[c] Treatment conditions: 80 °C, 2 h. After each treatment the sample was dried at 110 °C for 4 h.

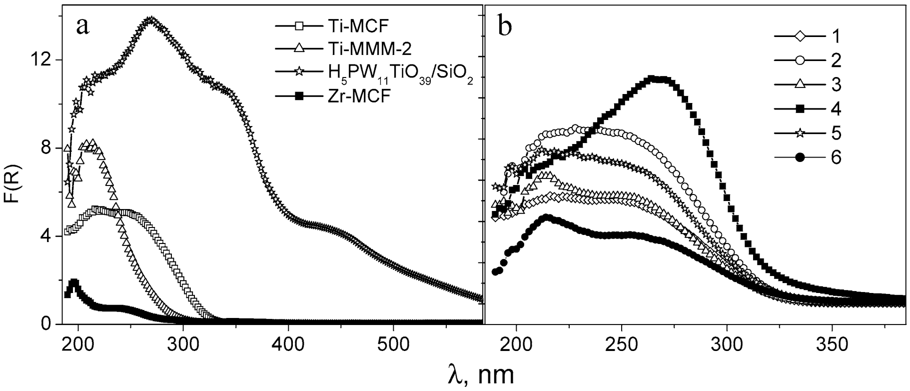

Fig. 2. DR-UV spectra for the catalysts used (a) and for the Ti-MCF after different treatments (b): (1) initial; (2) after calcination at 500 °C during 1 h; (3) after evacuation at 200 °C during 2 h; (4) after treatment with 30% H_2O_2 and drying at 110 °C during 1 h; (5) after treatment with 30% H_2O_2 and calcination at 500 °C during 1 h; (6) after treatment with 30% H_2O_2 and evacuation at 200 °C during 2 h. Treatment conditions: H_2O_2, 0.35 mmol, MeCN, 1 mL, 80 °C, 2 h.

band was broader and had two maxima, at 216 and 250 nm. The presence of the second maximum indicates that part of the titanium was in an octahedral, oligomerized, and/or highly hydrated form [36–38,40,42–44,48,72–76]. Significantly, evacuation of the sample resulted in decreased intensity of the second band (Fig. 2b). This indicates that at least a part of the titanium species was in a highly hydrated form, which could be reversibly transformed to the tetrahedral form. The TiO_2–SiO_2 mixed oxides showed a similar trend. The DR-UV spectrum of the Ti-MCF catalyst recorded after treatment with 30% aqueous H_2O_2 in MeCN showed a long-wave shift of the absorption band to 270 nm that disappeared after calcination and evacuation (Fig. 2b). Therefore, this shift can be attributed to the appearance of highly hydrated titanium species rather than partially oligomerized ones. The Fe-MMM-2 and Zr-MCF samples showed DR-UV bands with maxima at 221 and 197 nm, respectively, which can be assigned to isolated iron and zirconium species [56,77–79]. The DR-UV spectrum of $H_5PW_{11}TiO_{40}$/silica material was very close to the UV spectrum of $H_5PW_{11}TiO_{40}$ in water, indicating that the heteropoly acid structure remained unchanged during encapsulation in the silica matrix.

3.2. *Catalytic oxidation of α-pinene*

The results of the catalytic α-pinene oxidation with H_2O_2 along with blank experiments are presented in Table 3. According to GC-MS data, the main detectable oxidation products were verbenol, verbenone, and campholenic aldehyde. The product of α-pinene rearrangement, camphene, along with low molecular weight oligo/polymerization products, were also found by GC-MS. α-Pinene epoxide was not detected in the reaction mixtures, most likely due to its rapid further transformation to overoxidation products. Indeed, we observed rapid disappearance of the epoxide under the reaction conditions used, but found no campholenic aldehyde in the reaction mixture,

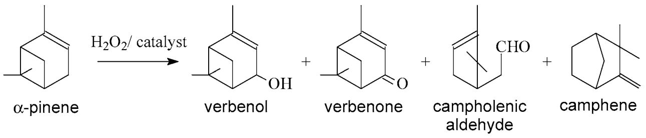

Table 3
α-Pinene oxidation with H_2O_2 in the presence of different catalysts[a]

Catalyst	α-Pinene conversion (%)	TOF_{av}[b] (h^{-1})	Yields[c] (%)			
			Camphene	Campholenic aldehyde	Verbenol	Verbenone
–	30	–	4	5	2	1
$H_5PW_{11}TiO_{40}$/silica	60	23.5	6	6	9	7
silica[d]	45	–	7	4	3	1
silica[d,e]	25	–	6	4	3	1
$H_5PW_{11}TiO_{40}$[f]	57	24.3	3	4	3	3
Ti-MMM-2	73	2.8	2	7	7	10
Ti-MCF	53	3.0	5	8	8	7
TiO_2–SiO_2-aerogel	54	1.1	5	8	9	8
TiO_2–SiO_2-xerogel	68	1.9	3	6	8	8
Zr-MCF	65	2.5	5	9	9	8
Fe-MMM-2	44	1.7	2	2	4	2

[a] Reaction conditions: α-pinene, 0.1 mmol, H_2O_2, 0.12 mmol, catalyst, 14 mg, MeCN, 1 mL, 50 °C, 5 h.

[b] $\text{TOF}_{av} = (\text{moles of } \alpha\text{-pinene consumed})/[(\text{moles of active metal}) \times 5\ \text{h})]$.

[c] GC yield based on initial α-pinene. Unidentified oligomeric/polymeric products also formed.

[d] Silica without Ti.

[e] Without H_2O_2. Unidentified hydrocarbons also formed (about 40% of the total amount of products).

[f] Homogeneous catalyst, 1.4 mg (4.7×10^{-4} mmol). Unidentified hydrocarbons also formed.

In the absence of catalyst and oxidant, α-pinene did not undergo any transformation. The α-pinene oxidation by H_2O_2 without catalyst resulted in 30% substrate conversion; however, the yield of desirable oxidation products, verbenol and verbenone, was very low. Both α-pinene conversion and verbenol/verbenone yield increased in the presence of all of the catalysts studied. Fe-MMM-2 was less active than Ti- and Zr-containing catalysts and gave lower yields of the target allylic oxidation products. The catalyst activity related to one Ti center (TOF_{av}) decreased in the following order: $H_5PW_{11}TiO_{40}$/silica > Ti-MCF > Ti-MMM-2 > Zr-MCF > Ti,Si-xerogel > Fe-MMM-2. The TOF value for the aerogel catalyst was rather low, whereas the α-pinene conversion and the product yield after 5 h were as high as those for the other Ti catalysts studied. This finding can be rationalized by taking into account the higher titanium loading in the aerogel material compared with the other samples. It is well known that increasing Ti content in a silicate matrix results in titanium oligomerization and decreasing activity with respect to one catalytic center [58,61,80]. This is in agreement with the shifting of the DRS-UV maximum to longer wavelengths observed for the aerogel sample (Table 1).

Surprisingly, the most active catalyst was the $H_5PW_{11}TiO_{40}$/silica composite material, despite its nonporous structure. The TOF values presented in Table 3 were calculated considering all of the Ti centers accessible. However, given the nonporous structure of the $H_5PW_{11}TiO_{40}$/silica material, we can suppose that only a minor part of the active centers (about 2%, according to our rough estimation) was really available for reactants, and thus the TOF value should be even higher for this material than the value given in Table 3. Evidently, the titanium center in $H_5PW_{11}TiO_{40}$/silica, where Ti(IV) is bound via bridging oxygens to four W(VI) ions and one P(V) ion, was more active than titanium dispersed in a silicate matrix. Recently, we reported that $H_5PW_{11}TiO_{40}$ heteropoly acid is a highly active catalyst in H_2O_2-based oxidation of cyclohexene [81]. It is noteworthy that despite the nonporous structure, the heterogeneous $H_5PW_{11}TiO_{40}$/silica catalyst was as active as homogeneous $H_5PW_{11}TiO_{40}$. Moreover, the heterogeneous catalyst was more selective to allylic oxidation products than the homogeneous catalyst (Table 3). To estimate the effect of support on the α-pinene oxidation, we carried out the experiments with pure silica prepared by the sol–gel method. Our results indicate that silica itself promoted α-pinene isomerization to camphene both in the presence and in the absence of H_2O_2.

We studied the factors governing the selectivity of α-pinene allylic oxidation using the Ti-MCF and $H_5PW_{11}TiO_{40}$/silica catalysts. Both materials are rather new, and to the best of our knowledge, their catalytic properties in H_2O_2-based selective oxidations have not yet been studied. We focused also our attention on these two materials because their selectivity with respect to verbenol/verbenone formation was higher than the selectivity with the other materials studied. The yields of verbenol and verbenone with TiO_2–SiO_2 aerogel and xerogel were close to those obtained with Ti-MCF. However, it is well known that TiO_2–SiO_2 mixed oxides suffer from hydrolytic instability when aqueous H_2O_2 is used as an oxidant [47,48,61]. In contrast, this work demonstrates a relative stability of the porous structure of Ti-MCF (see Table 2).

Table 4
Effect of the solvent properties on the catalyst activity/selectivity[a]

Catalyst	Solvent	$[H_2O]$ (M)	α-Pinene conversion (%)	Yield (%)	
				Verbenol	Verbenone
$H_5PW_{11}TiO_{40}$/silica	Acetonitrile	–[b]	53	8	7
$H_5PW_{11}TiO_{40}$/silica	Acetonitrile	0.5	60	9	7
$H_5PW_{11}TiO_{40}$/silica	Acetonitrile	0.8	49	9	7
$H_5PW_{11}TiO_{40}$/silica	Acetone	0.5	38	2	1
$H_5PW_{11}TiO_{40}$/silica	Toluene[c]	0.5	15	1	1
Ti-MCF	Acetonitrile	0.5	53	8	7
Ti-MCF	Acetonitrile	0.8	62	14	12
Ti-MCF	Acetone	0.5	44	1	3
Ti-MCF	Toluene[c]	0.5	20	2	1

[a] Reaction conditions: α-pinene, 0.1 mmol, H_2O_2, 0.12 mmol, catalyst, 14 mg, solvent, 1 mL, 50 °C, 5 h.

[b] Unhydrous hydrogen peroxide urea adduct was used instead of aqueous H_2O_2.

[c] Three-phase system: toluene/H_2O/catalyst.

The solvent nature impacts both catalyst activity and selectivity, which decrease in the following order: acetonitrile > acetone > toluene (a three-phase system in the latter case) (Table 4). Increasing the concentration of hydrogen peroxide from 0.12 to 0.2 M slightly increased the achievable substrate conversion, but had practically no influence on the product yield. Adding water favored formation of the allyl oxidation products when Ti-MCF was used as the catalyst. In contrast, adding or removing water (experiment with nonhydrous H_2O_2-urea adduct) produced very little effect on the $H_5PW_{11}TiO_{40}$/silica-catalyzed oxidation (Table 4).

The kinetic curves for α-pinene consumption and verbenol/verbenone formation are shown in Fig. 3. Their character indicates that verbenol and verbenone form via parallel routes, and that the ketone does not derive from the alcohol. An independent experiment with verbenol oxidation under typical reaction conditions at 50 °C corroborated this suggestion. Verbenol rapidly disappeared to yield overoxidation products, but no verbenone was found among them. The rate of both α-pinene consumption and verbenol/verbenone for-

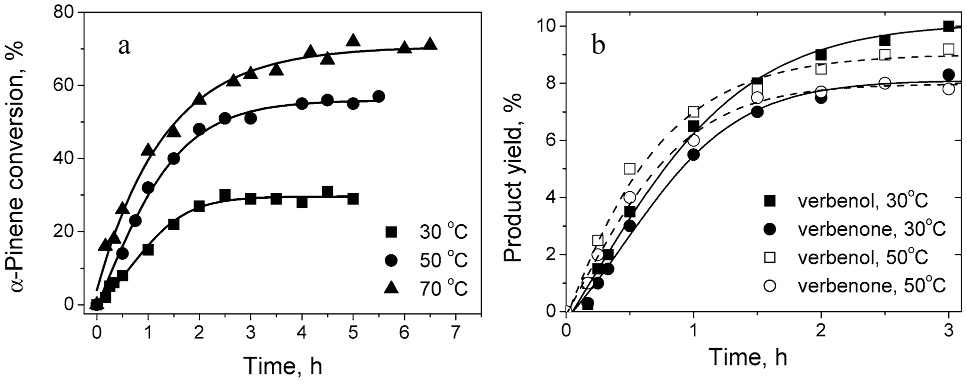

Fig. 3. Effect of temperature on the reaction course (a) and product yield (b). Reaction conditions: α-pinene, 0.1 mmol, H_2O_2, 0.12 mmol, $H_5PW_{11}TiO_{40}$/silica, 14 mg (4.4×10^{-4} mmol Ti), MeCN, 1 mL.

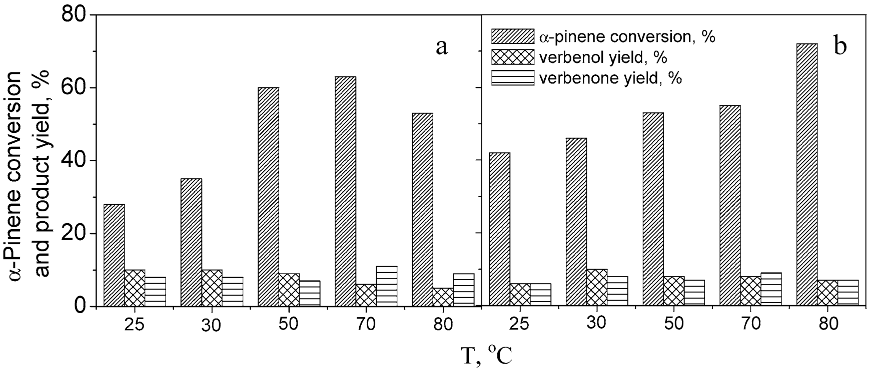

Fig. 4. Effect of temperature on the α-pinene conversion/product yield in the presence of $H_5PW_{11}TiO_{40}$/silica (a) and Ti-MCF (b). Reaction conditions: α-pinene, 0.1 mmol, H_2O_2, 0.12 mmol, catalyst, 14 mg, MeCN, 1 mL, 5 h.

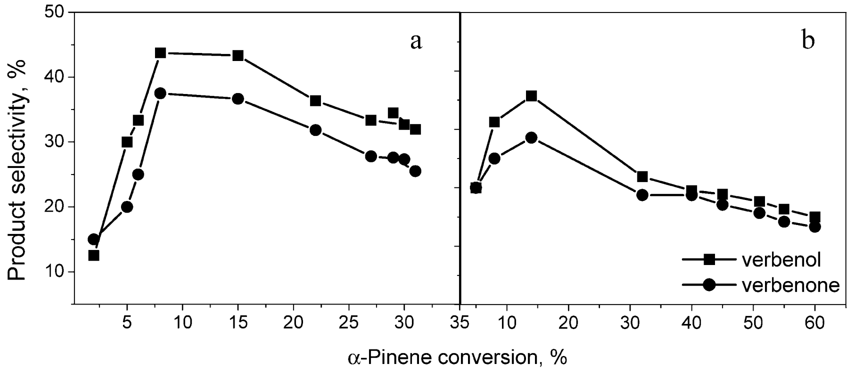

Fig. 5. Effect of α-pinene conversion and temperature on verbenol/verbenone selectivity at 30 (a) and 50 °C (b). Reaction conditions: α-pinene, 0.1 mmol, H_2O_2, 0.12 mmol, $H_5PW_{11}TiO_{40}$/silica, 14 mg (4.4×10^{-4} mmol Ti), MeCN, 1 mL.

mation increased with increasing temperature (Fig. 3). The feasible α-pinene conversion, and thus the H_2O_2 efficiency, increased with increasing temperature, indicating that unproductive decomposition of H_2O_2 is likely less pronounced at elevated temperatures compared with α-pinene oxidation. The same regularity was also observed for Zr-MCF. The total verbenol/verbenone yield at a settled reaction time (5 h) did not change significantly with changes in temperature, whereas the molar ratio of verbenol/verbenone decreased once the temperature exceeded 50 °C (Fig. 4). Again, the latter effect was not due to conversion of verbenol to verbenone. Selectivity toward verbenol/verbenone depends strongly on α-pinene conversion and the reaction temperature (Fig. 5). At 30 °C, the total selectivity toward verbenol/verbenone reached the maximal value of 80–82% at 8–15% conversion of the substrate and then declined (Fig. 5a) due to the overoxidation processes, leading to oligomeriztion/polymerization products. At 50 °C, the maximal attainable selectivity to verbenol/verbenone at the same conversion level was lower (Fig. 5b).

Both H_2O_2 efficiency and verbenol/verbenone yield increased with increasing α-pinene/H_2O_2 molar ratio (Fig. 6). Thus the total yield of verbenol and verbenone based on H_2O_2 was 5% at a molar ratio of 0.42 and 28% at a molar ratio of 1.67. The augmenting catalyst content accelerated α-pinene oxidation and had very little effect on verbenol/verbenone yield.

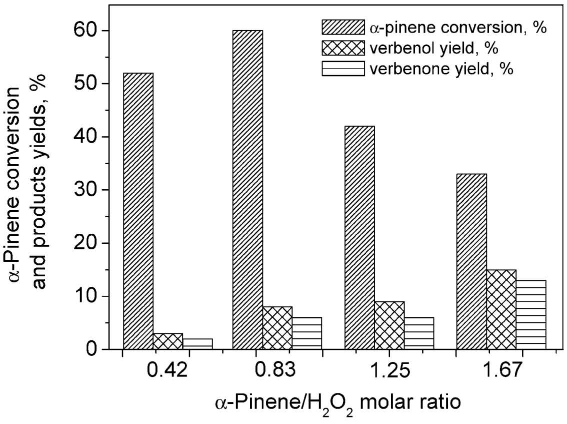

Fig. 6. Effect of the α-pinene/H_2O_2 molar ratio on the α-pinene conversion/product yield. Reaction conditions: α-pinene, 0.05–0.2 mmol, H_2O_2, 0.12 mmol, $H_5PW_{11}TiO_{40}$/silica, 14 mg (4.4×10^{-4} mmol Ti), MeCN, 1 mL, 50 °C, 5 h.

3.3. *Catalyst stability and recycling*

The important questions that must be addressed while studying liquid phase oxidation processes over a solid catalyst involve catalyst stability to leaching of the active component and other transformations, the true heterogeneity of the oxidation process, and the possibility of catalyst recycling. Previously we demonstrated that mesoporous titanium silicates of different natures behave as true heterogeneous catalysts in a

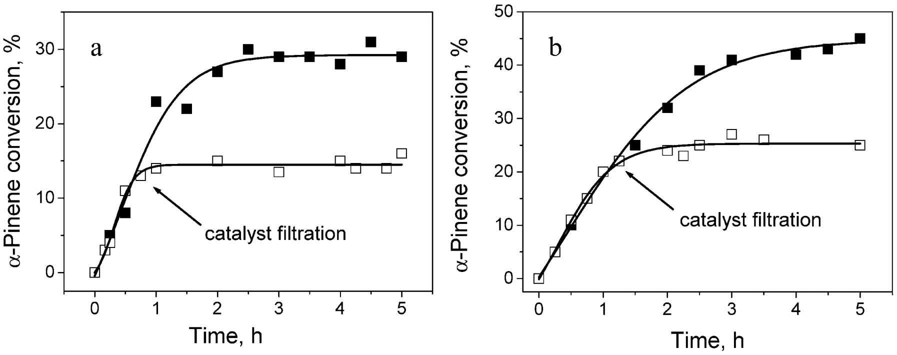

Fig. 7. Oxidation of α-pinene with H_2O_2 over $H_5PW_{11}TiO_{40}$/silica (a) and Ti-MCF (b). Reaction conditions: α-pinene, 0.1 mmol, H_2O_2, 0.12 mmol, catalyst, 14 mg, MeCN, 1 mL, 30 °C.

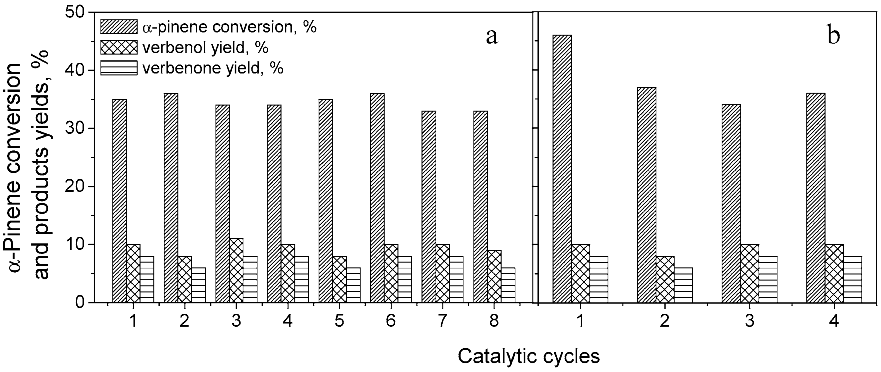

Fig. 8. Catalyst recycling: $H_5PW_{11}TiO_{40}$/silica (a) and Ti-MCF (b). Reaction conditions: α-pinene, 0.1 mmol, H_2O_2, 0.12 mmol, catalyst, 14 mg, MeCN, 1 mL, 30 °C, 5 h.

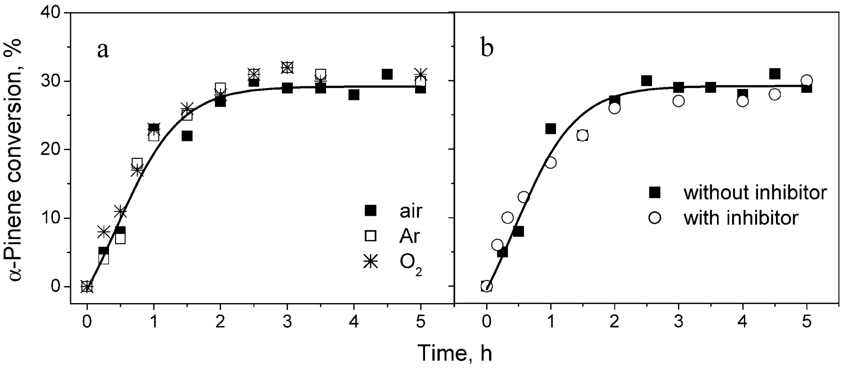

Fig. 9. Effects of the reaction atmosphere (a) and additive of inhibitor (2,6-di-*tert*-butyl-*p*-methylphenol, 0.002 mmol) (b) on the reaction course. Reaction conditions: α-pinene, 0.2 mmol, H_2O_2, 0.24 mmol, catalyst, 28 mg (0.001 mmol Ti), MeCN, 2 mL, 30 °C.

number of selective oxidations with H_2O_2 when MeCN was used as a solvent; no titanium leaching was observed [58,61]. Meanwhile, most of these catalysts lost some activity due to damage of the porous structure and partial oligomerization of titanium, which typically occurred on the catalyst surface in the presence of aqueous H_2O_2 [49,53,58]. The exception was the recently developed Ti-MMM-2 catalyst, the macrostructure and microstructure of which do not suffer from water and H_2O_2/MeCN [63]. Using the commonly accepted methodology of studying the stability of solid catalysts in liquid phase oxidations, we investigated the Ti-MCF and $H_5PW_{11}TiO_{40}$/silica catalysts. The experiments with fast catalyst filtration performed at the reaction temperature demonstrated no further α-pinene conversion in the filtrate after catalyst removal (Fig. 7). This proves that both $H_5PW_{11}TiO_{40}$/silica and Ti-MCF operate as truly heterogeneous catalysts. Even if very small amounts of the titanium species are leached from the solid matrix during the oxidation process, the observed catalytic activity is not due to these species. Additionally, elemental analysis data showed that the titanium content remains constant after at least three catalytic cycles (Table 1).

The catalyst recycling was examined for both $H_5PW_{11}TiO_{40}$ /silica and Ti-MCF (Fig. 7). The $H_5PW_{11}TiO_{40}$/silica composite material lost practically no activity and selectivity during at least eight catalytic cycles (Fig. 8a). In contrast, the activity of Ti-MCF (α-pinene conversion after 5 h) decreased after the first use, whereas the verbenol/verbenone yields remained unchanged (Fig. 8b). We may assume that some decrease in the activity of Ti-MCF is due to the formation of hydrated titanium species in the presence of H_2O_2 (vide supra). Importantly, the yields of the target products, verbenol and verbenone, do not suffer from this partial titanium oligomerization, in sharp contrast to what we had observed earlier for the H_2O_2-based oxidation of 2,3,6-trimethylphenol over Ti,Si catalysts [58,61].

Formation of the allylic oxidation products in α-pinene oxidation over Ti-containing catalysts indicates that the reaction proceeds via a homolytic mechanism [82]. If the reaction proceeded via a heterolytic oxygen transfer, then the predominate formation of α-pinene epoxide and its rearrangement products would be expected. We found that the reaction atmosphere (air, O_2, or Ar) and small amounts of the radical chain inhibitor, 2,6-di-*tert*-butyl-p-methylphenol, did not affect the reaction rate (Fig. 9) and product yield. All of these facts collectively support a radical nonchain mechanism of the α-pinene oxidation or a mechanism that involves short chains [83].

4. Conclusion

The new composite $H_5PW_{11}TiO_{40}$/silica material prepared by the sol–gel technique, as well as Ti-MCF, are efficient catalysts for allylic oxidation of α-pinene to a verbenol/verbenone mixture. The product selectivity depends strongly on the solvent nature, substrate to oxidant molar ratio, reaction temperature, and α-pinene conversion. The oxidation is a true heterogeneous process. In MeCN, at 30 °C, with the $H_5PW_{11}TiO_{40}$/silica catalyst, the selectivity toward verbenol/verbenone attains 80–82% at 8–15% conversion of the substrate and 68% at 28% conversion. The $H_5PW_{11}TiO_{40}$/silica can be used repeatedly without a significant loss in activity, whereas Ti-MCF activity decreases after the first use; no leaching of the active component is observed. The reaction most likely proceeds via a radical nonchain mechanism.

Acknowledgments

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