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ScienceDirect
Journal of Catalysis 246 (2007) 241–248
JOURNAL OF CATALYSIS
www.elsevier.com/locate/jcat

Aerobic oxidations of α-pinene over cobalt-substituted polyoxometalate supported on amino-modified mesoporous silicates

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Received 6 October 2006; revised 22 November 2006; accepted 22 November 2006

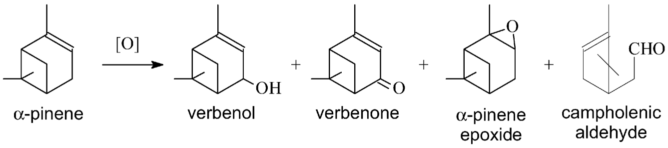
Abstract

Co-containing polyoxometalate $[Bu_4N]_4H[PW_{11}Co(H_2O)O_{39}]$ (Co-POM) was supported on various NH_2-modified mesoporous silicate matrixes (SBA-15, MCF, and SiO_2-xerogel). The catalysts were characterized by elemental analysis, N_2 adsorption, DRS–UV, and FTIR spectroscopy. α-Pinene autoxidation and its co-oxidation with isobutyraldehyde (IBA) over the supported Co-POM catalysts have been studied and compared with the corresponding processes in the presence of the homogeneous Co-POM. The autoxidation process affords allylic oxidation products, the selectivity to verbenol/verbenone decreases with alkene conversion and attains 70% at 20% conversion and 40% at 46% conversion. The catalysts can be used repeatedly without loss of the activity and selectivity during several catalytic cycles. Co-oxidation of α-pinene and IBA produces selectively α-pinene epoxide with up to 94% selectivity at 96% alkene conversion. The catalysts can be regenerated by evacuation.

Keywords: α-Pinene; Autoxidation; Verbenol; Verbenone; Isobutyraldehyde; α-Pinene epoxide; Co(II); Polyoxometalate; Mesoporous silicate supports

1. Introduction

α-Pinene is a cheap and readily available starting material for the production of various flavors, fragrances, agrochemicals, and therapeutically active substances [1,2]. Particularly, its oxygenated derivatives, verbenol, verbenone, α-pinene epoxide, and campholenic aldehyde, are of high practical importance as flavor chemicals and precursors of a range of fine chemicals, including citral, menthol, sandalwood fragrance santalol, and taxol, as well as vitamins A and E [1–7]:



The development of catalytic methods for the selective α-pinene oxidation by "green" oxidants is a challenging goal of fine chemistry. Molecular oxygen is the most attractive oxidant because it is readily available, cheap, atom-efficient, and environmentally benign.

The autoxidation of α-pinene produces the allylic oxidation products verbenol and verbenone with a rather low total selectivity [8–10]. Transition metals, in general, and cobalt, salts, and complexes in particular, facilitate this reaction and improve the selectivity [11–21]. The maximal verbenol/verbenone selectivity (76%) was reported for homogeneous catalysts, $Co(NO_3)_2$ and $Co(4\text{-}MeC_5H_3N)_2Br_2$ [16–18]. Several attempts to heterogenize cobalt-containing catalysts effective in α-pinene oxidation were made, including encapsulation of Co(II)Saloph complexes in zeolite-Y [12] and immobilization of $Co(NO_3)_2$ in silica matrix by the sol–gel method [21]. Harsh reaction conditions [100 °C/30 atm O_2 for Co(II)Saloph-Y and 60 °C/10 atm O_2 for Co/SiO_2], along with rather low Co/SiO_2 activity (40% substrate conversion after 24 h) are disadvantages of these catalytic systems. No leaching of the active metal was

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0021-9517/$ – see front matter
doi:10.1016/j.jcat.2006.11.026

announced, but no elemental analysis data and catalysts recycling tests were reported to demonstrate the catalyst stability.

At the beginning of 1990s, Mukayama et al. found that highly selective olefin epoxidation can be carried out under mild reaction conditions (1 atm of O_2 or air at room temperature) using a very simple catalytic combination, such as transition metal complex/branched aliphatic aldehyde/O_2 [22–38]. Cobalt(II) complexes [25–27,33], including cobalt-containing polyoxometalates [29,34,37], were among the most active catalysts for alkene/isobutyraldehyde (IBA) co-oxidation. Importantly, this method can be applied even for the production of acid-sensitive epoxides. The selective α-pinene epoxidation via co-oxidation with branched aliphatic aldehydes has been reported to proceed efficiently in the presence of both homogeneous Ni(II) and Co(II) catalysts [11,14,25,26,33,38], as well as over solid CoNaY [39]; however, the latter was not stable with respect to leaching of cobalt under the reaction conditions.

Transition metal-substituted polyoxometalates are attracting much attention as oxidation catalysts because of their numerous unique properties, including metal oxide-like structure and thermodynamic stability to oxidation [40–49] and their ability to be supported on different porous materials [50–61], for example, attached to NH_2-modified silica surfaces by dative [55] or electrostatic binding [51,54,61]. Supported materials, such as $H_5PV_2Mo_{10}O_{40}$/MCM-41 [51,54], $[M^{II}(H_2O)PW_{11}O_{39}]^{5-}$/silica (M = Co, Zn) [55], and $[SiW_9O_{37}\{Co^{II}(H_2O)\}_3]^{10-}$/silica [55], revealed stable catalytic properties in two cycles of cyclooctane oxidation [54] and olefin/IBA co-oxidation [51,55]. However, no elemental analysis data and experiments with fast catalyst filtration were provided to confirm the lack of leaching under the reaction conditions. Recently, we found that Co-POM and $[PW_{11}CoO_{39}]^{5-}$ immobilized on amine-modified xerogel by electrostatic binding are active catalysts in aldehyde oxidation with dioxygen but suffer from leaching [61].

In this work, we attempted to improve the catalytic performance, including stability, of the supported Co-POM catalysts by using hydrothermally stable silicate supports, such as mesoporous cellular foams (MCFs) and mesostructured material SBA-15 modified by amino groups. The catalytic properties of the obtained materials were assessed in α-pinene autoxidation and its co-oxidation with isobutyraldehyde. Special attention was paid to catalyst stability and recyclability.

2. Experimental

2.1. Materials

α-Pinene, containing 98% of α-pinene and 2% of β-pinene, was obtained by vacuum rectification of gum turpentine. Isobutyraldehyde was purchased from Fluka and distilled before each experiment. All other reactants were obtained commercially and used without further purification.

Tetrabutylammonium salt of Co-POM, $[TBA]_4H[PW_{11}Co(H_2O)O_{39}]$ (TBA = Bu_4N), was prepared by metathesis of $Na_5PW_{11}CoO_{39}$ with TBABr in water at pH 2.7 as described previously [61]. The number of protons in Co-POM was determined by potentiometric titration with methanolic TBAOH (Aldrich).

2.2. Catalyst preparation and characterization

2.2.1. NH_2-functionalized mesoporous materials

Synthesis of SBA-15 silicate was carried out by a sol-“mesophase” route [62]. Briefly, a silica sol prepared from $Na_2Si_2O_5$ and 4 M HCl solutions ($Si^{4-}/H^+ = 0.9$) was added to a 0.02 M solution of Pluronic P123 (Aldrich) in water. The resulting mixture was stirred for 5 h, and then its pH was adjusted to 2.5. A composition of the mixture was $Na:Si:Cl:H_2O = 1:1:1.1:160$. The mixture was placed into an autoclave and aged overnight at 120 °C. Finally, it was filtered off, and the resulting precipitate was washed in distilled water, dried overnight, and calcined at 550 °C. Synthesis of NH_2-SBA-15 was carried out as described previously [63,64]. Dried SBA-15 silicate (1 g) was dispersed in 50 mL of *o*-xylol under helium, after which 1.5 g of 3-aminopropyltriethoxysilane was added. This mixture was refluxed for 2 h. The NH_2-SBA-15 thus obtained was filtered out and dried under vacuum at room temperature for 24 h. The resulting NH_2-SBA-15 contained 0.64 mmol NH_2 per 1 g of SiO_2.

NH_2-functionalized mesoporous xerogel was prepared using 10 mol% of 3-aminopropyltriethoxysilane and ethyl silicate 40 as silica precursors as described previously [61]. The molar ratio of reagents was $Si:H_2O:EtOH:NH_3 = 1:3:9:0.008$. The resulting NH_2-xerogel contained 1.15 mmol of NH_2 per 1 g of SiO_2.

The structure of siliceous MCF was templated by oil in water microemulsions as described previously [65]. 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 NH_2-MCF sample was obtained by a procedure similar to that described for NH_2-SBA-15 using 10 mol% of $(CH_3O)_3Si(CH_2)_3NHCH_2CH_2NH_2$. The resulting NH_2-MCF support contained 2.59 mmol of NH_2 per 1 g of SiO_2.

2.2.2. Immobilization of Co-POMs

The supported Co-POM samples were prepared by dissolving 157 mg of Co-POM in MeCN (3 mL), adding 326 mg of a support (NH_2-X), stirring for a few hours, storing overnight at room temperature, filtering, washing with MeCN until the filtrate becomes colorless, and then drying in air until the weight remains constant.

The Co-POM/SiO_2 composite material was prepared by the sol–gel method using $Na_5PW_{11}CoO_{39}$ (10 wt%) and tetramethoxysilane as described previously [61]. The molar ratio of reagents was $Si:H_2O:MeOH:HCl = 1:12:9:0.0016$.

The textural characteristics of the catalysts were determined from nitrogen adsorption isotherms. The catalysts were also characterized by elemental analysis (nitrogen and cobalt content), DR–UV, and FTIR spectroscopy.

2.3. Catalytic oxidations

Catalytic experiments were carried out in thermostatted glass vessels under vigorous stirring at 50 °C for α-pinene autoxidation and at 25 °C for α-pinene and IBA co-oxidation. Typically, 0.1 mmol of α-pinene (and 0.4 mmol IBA in the case of α-pinene and IBA co-oxidation) was added to a preliminary blown with oxygen mixture containing catalyst (6×10^{-4} mmol Co), internal standard (biphenyl), and 1 mL of acetonitrile. Aliquots of the reaction mixture were withdrawn periodically during the reaction course by syringe through a septum. Each experiment was reproduced 2 to 3 times. The reaction products were identified by GC–MS and quantified by GC. After the reactions, catalysts were filtered off, washed with acetonitrile and methanol, dried in air at room temperature overnight (treatment A) or evacuated at 130 °C for 2 h (treatment B), and then reused.

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 a Agilent 6890 gas chromatograph with a quartz capillary column (30 m × 0.25 mm/HP-5 ms) equipped with an Agilent MSD 5973 quadrupole mass-selective detector. DRS–UV measurements were performed on a Shimadsu UV–vis 2501PC spectrophotometer at ambient conditions. FTIR spectra were recorded using KBr pellets containing 0.3 wt% of sample on a BOMEM-MB-102 spectrometer in 250–4000 cm^{-1} range. Nitrogen adsorption isotherms at 77 K were measured using a Quantachrome Autosorb-6BKr.

3. Results and discussion

3.1. Catalysts preparation and characterization

To obtain immobilized Co-POM catalysts, we used an approach [61], which is based on the electrostatic binding between $[\text{TBA}]_4\text{H}[\text{PW}_{11}\text{CoO}_{39}]$ and X-NH_2,

$$\text{X-NH}_2 + \text{H-POM} = \text{X-NH}_3^+\text{POM}^-. \quad (1)$$

The elemental analysis data and textural properties of the initial supports (NH_2-X) and supported Co-POM samples are given in Tables 1 and 2, respectively. The Co-POM loading depended on the surface concentration of NH_2 groups on the support. Both the surface area and pore volume decreased on Co-POM deposition, but the average mesopore diameter did not change. FTIR studies were performed to check whether the Co-POM structure was preserved in the supported samples similar to how it was retained for Co-POM/SiO_2 mesoporous xerogel and Co-POM/SiO_2 microporous composite materials [61]. The IR spectra of Co-POM/NH_2-MCF and Co-POM/NH_2-SBA-15 samples were similar after subtracting the peaks of the supports (Fig. 1). Some small differences in the spectra are most likely due to an element of uncertainty in the subtraction procedure. Importantly, the IR spectra of the supported Co-POMs exhibit the principal stretching modes of the Keggin Co-POM unit (956, 888, 818, 752, and 720 cm^{-1}), which is a clear indicative of the maintenance of the heteropolyanion structure after immobilization.

Table 1
Elemental analyses data for supported Co-POM catalysts

Catalyst	Co[a] (wt%)	Co-POM (wt%)	NH_2 (mmol/g SiO_2)	NH_2/Co-POM (mol/mol)
Co-POM/NH_2-SBA-15	0.24 (0.10)	15	0.64	16
Co-POM/NH_2-xerogel	0.31 (0.08)	20	1.15	21
Co-POM/NH_2-MCF	0.51 (0.28)	32	2.59	30
Co-POM/SiO_2	0.08	4	–	–

[a] Weight percent of Co in the sample; inside parentheses, the wt% of Co after five catalytic cycles of α-pinene and IBA co-oxidation; the reaction conditions are given in Table 4. After the reactions, catalysts were filtered off, washed with acetonitrile and methanol, dried in air at room temperature overnight and re-used.

Table 2
Textural properties of supported Co-POM catalysts

Sample	A[a] (m^2/g)	V_p[b] (cm^3/g)	d_p[c] (nm)
NH_2-SBA-15	623	1.34	13
Co-POM/NH_2-SBA-15	418 (420)[d]	1.15 (1.14)[d]	13
NH_2-xerogel	540	1.24	12–16[e]
Co-POM/NH_2-xerogel	510 (520)[d]	1.09 (1.02)[d]	12–16[e]
NH_2-MCF	625	2.82	15
Co-POM/NH_2-MCF	440 (400)[d]	1.40 (1.35)[d]	15 (14)[d]
Co-POM/SiO_2[f]	360	0.17	1.5

[a] Mesopore surface area.

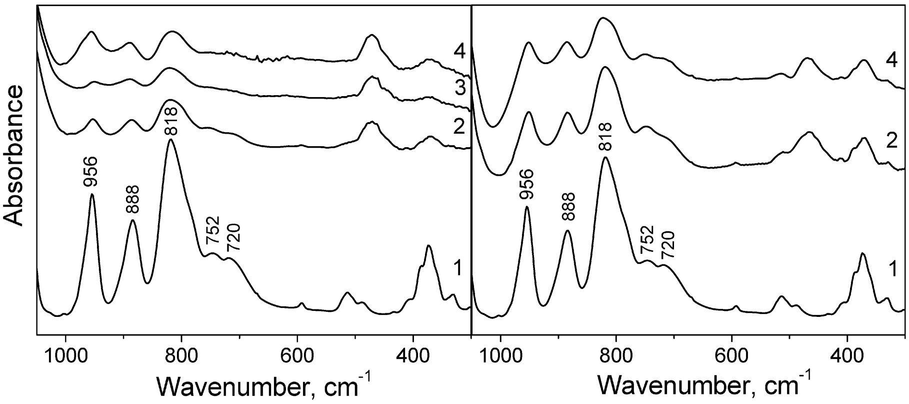
[b] Mesopore volume.

[c] Average mesopore diameter.

[d] Inside parentheses, the values after five catalytic cycles of α-pinene and IBA co-oxidation (the reaction conditions are given in Table 4; after the reactions, catalysts were treated as described in the footnote to Table 1).

[e] A broad mesopore distribution.

[f] Microporous material.



(a) (b)

Fig. 1. FTIR spectra of (a) Co-POM/NH_2-SBA-15 and (b) Co-POM/NH_2-MCF after subtraction of the spectrum of the corresponding support: 1—Co-POM; 2–4—supported Co-POM catalysts before reaction, after one and five catalytic cycles of α-pinene and IBA co-oxidation, respectively. For the reaction conditions, see Section 2 (treatment A).

The DRS–UV–vis study was carried out to characterize further the supported Co-POMs. The band assignment in UV–vis spectra and interpretation of the electronic state of metal ions in the Keggin type Co-POMs, including $PW_{11}Co^{II}(L)O_{39}^{5-}$, was given previously [66]. The UV–vis spectra (*d–d* transitions) are sensitive to the nature of the solvent and, in turn, the nature of the ligand L on the sixth external position of Co(II) [66]. Co-POMs datively linked to NH_2-silica reveal peaks or shoulders in the range of 628–640 nm, indicating the formation of dative bonds between NH_2 groups and cobalt(II) [55].

Fig. 2 shows the DRS–UV–vis spectra of the initial Co-POM and supported Co-POM/NH_2-MCF before and after catalytic reaction. The spectra for the other supported Co-POM catalysts were alike. It is worth of noting that the spectrum of the supported Co-POM is quite similar to that of the initial $[TBA]_4H[PW_{11}Co(H_2O)O_{39}]$ (Fig. 2) and to the spectra of Co-POM electrostatically linked to amorphous NH_2-silica [61]. Importantly, no peaks or shoulders were observed in the range of 628–640 nm, indicating no transitions due to dative bonds between NH_2 groups and cobalt(II) [55]. This indicates the electrostatic binding between Co-POM and the support. Yet one more argument in favor of the coulomb nature of the interaction between Co-POM and –NH_3^+ groups of the silica supports is the fact that the catalyst containing immobilized Co-POM (pale pink) becomes colorless after treatment with a 1 M solution of $TBAClO_4$ in MeCN. In addition, the elemental analysis data confirm Co-POM leaching from the solid matrix after such treatment.

3.2. Catalytic oxidation of α-pinene

In the absence of catalyst and oxidant, α-pinene did not undergo any transformations. All of the Co-POM-containing materials catalyzed both the α-pinene oxidation by O_2 and α-pinene co-oxidation with IBA. The results of the catalytic α-pinene oxidation with O_2 and its co-oxidation with IBA, along with blank experiments, are presented in Tables 3 and 4, respectively. According to GC–MS data, the main detectable oxidation products of the catalytic α-pinene autoxidation were verbenol and verbenone. The product of α-pinene rearrangement, camphene, along with low-molecular-weight oligo/polymerization products, were found by GC–MS. α-Pinene co-oxidation with IBA gave selectively α-pinene epoxide and isobutyric acid:

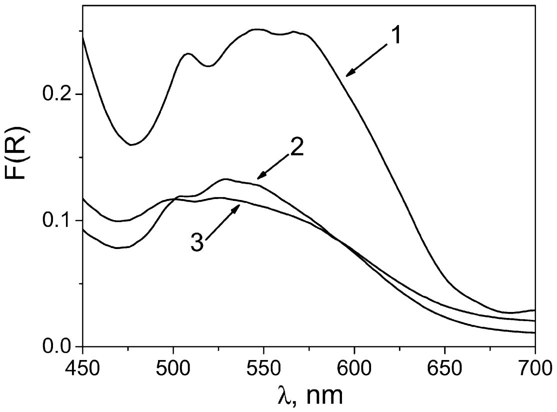
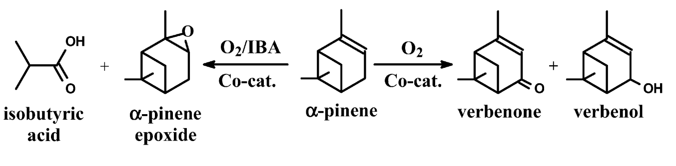


Fig. 2. DRS–UV spectra of (1) $[Bu_4N]_4H[PW_{11}Co(H_2O)O_{39}]$ and Co-POM/NH_2–MCF: (2) before reaction and (3) after five catalytic cycles of α-pinene and IBA co-oxidation. For the reaction conditions, see Section 2 (treatment A).



The catalyst activity related to one Co center (TOF) was almost equal for all of the samples studied. Importantly, the activity of the supported Co-POM catalysts was comparable to the activity of the homogeneous Co-POM. Furthermore, the supported samples were even more selective in the case of α-pinene and IBA co-oxidation. To estimate the effect of the support on α-pinene oxidation, we carried out the experiments with Co-POM-less NH_2-SBA-15. It is worth of noting that the support itself shows some inhibiting properties. Thus, α-pinene conversion after 5 h was 60% and 40% in the blank experiment of α-pinene and IBA co-oxidation in the absence and in the

Table 3
α-Pinene autoxidation in the presence of supported Co-POM catalysts[a]

Catalyst	α-Pinene conversion (%)	TOF[b] (h^{-1})	Yield[c] (%)		
			Campholenic aldehyde	Verbenol	Verbenone
–[d]	15		2	5 (33)	4 (27)
Co-POM[e]	45	50	9	16 (36)	11 (24)
NH_2-SBA-15	13		2	3 (23)	2 (15)
CO-POM/NH_2-SBA-15	46	50	7	12 (26)	6 (13)
Co-POM/NH_2-xerogel	48	55	7	11 (23)	8 (17)
Co-POM/SiO_2[f]	42	135	8	15 (36)	11 (26)
Co-POM/NH_2-MCF	43	50	7	10 (23)	6 (14)

[a] Reaction conditions: α-pinene, 0.1 mmol; O_2, 1 atm; catalyst, 6×10^{-4} mmol Co-POM; MeCN, 1 mL; 50 °C, 1 h.
[b] TOF = (moles of α-pinene consumed in the catalytic reaction − moles of α-pinene consumed in the blank experiment)/[(moles of Co) × 1 h].
[c] GC yield based on initial α-pinene (inside parentheses, CG yield based on α-pinene consumed); unidentified oligomeric/polymeric products also formed.
[d] No catalyst was present.
[e] Homogeneous catalyst, 2.1 mg (6×10^{-4} mmol Co-POM).
[f] 2×10^{-4} mmol Co-POM.

Table 4
α-Pinene co-oxidation with IBA in the presence of Co-POM catalysts[a]

Catalyst	α-Pinene conversion (%)	TOF[b] (h^{-1})	Yield[c](%)	
			Campholenic aldehyde	α-Pinene epoxide
–[d]	4		Traces	Traces
Co-POM[e]	77	130	8 (10)	67 (87)
NH_2-SBA-15	5		Traces	Traces
Co-POM/NH_2-SBA-15	95	160	15 (16)	72 (76)
Co-POM/NH_2-xerogel	98	160	11 (11)	62 (63)
Co-POM/SiO_2[f]	85[g]	220	13 (15)	62 (73)
Co-POM/NH_2-MCF	96[g]	90	8 (8)	90 (94)

[a] Reaction conditions: α-pinene, 0.1 mmol; IBA, 0.4 mmol; O_2, 1 atm; catalyst, 6×10^{-4} mmol Co-POM; MeCN, 1 mL; 25 °C, 1 h.
[b] TOF = (moles of α-pinene consumed)/[(moles of Co) ×1 h].
[c] GC yield based on initial α-pinene (inside parentheses, CG yield based on α-pinene consumed).
[d] No catalyst was present.
[e] Homogeneous catalyst, 2.1 mg (6×10^{-4} mmol Co-POM).
[f] 2×10^{-4} mmol Co-POM.
[g] After 2 h.

presence of the support, respectively. The same tendency was observed for the autoxidation reaction. This allowed us to assume that the support can catch active radicals.

We have found that the nature of the support hardly affects the selectivity of α-pinene autoxidation, which is a bit lower compared with homogeneous Co-POM. The total verbenol/verbenone selectivity reached 37–40% at 43–48% substrate conversion after 1 h reaction, except for Co-POM/silica composite material, for which the total verbenol/verbenone selectivity was as high as 62% at 42% substrate conversion. The allylic oxidation products selectivity depended strongly on the α-pinene conversion. The total selectivity toward verbenol/verbenone reached the maximal value of 60–70% at 16–20% conversion of the substrate and then declined (Fig. 3) due to overoxidation processes leading to oligomerization/polymerization products.

The use of catalysts allows to obtain target products with higher selectivity and to use milder reaction conditions [8–10, 67]. In α-pinene autoxidation, the verbenol/verbenone selectivity reached 54% at 16% substrate conversion at 100 °C and 4 atm O_2 [67], whereas α-pinene oxidation over supported Co-POMs led to the formation of allylic oxidation products (verbenol and verbenone) with total selectivity of 70% at 20% substrate conversion at 50 °C and 1 atm O_2. Supported Co-POM catalysts are more active/selective in α-pinene allylic oxidation than the known heterogeneous Co-containing catalysts [12,21], require milder reaction conditions, and are more stable [39].

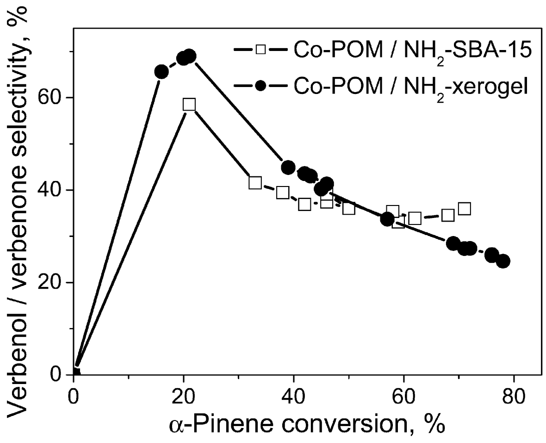


Fig. 3. Effect of α-pinene conversion on verbenol/verbenone selectivity. For the reaction conditions, see Section 2.

In the case of α-pinene and IBA co-oxidation, the supported Co-POM catalysts were found to be more selective than the corresponding homogeneous Co-POM. Yet, in contrast to autoxidation, the selectivity of α-pinene/IBA co-oxidation may be altered by varying the amount of NH_2 groups. Thus, the Co-POM/NH_2-MCF sample was the most selective catalyst; α-pinene epoxide selectivity reached 94% at 96% substrate conversion after 2 h. This may be explained by a larger surface concentration of NH_2 groups in this sample, which may partially neutralize the carboxylic acid formed during the reaction.

3.3. *Catalyst stability and recycling*

The important questions that must be addressed while studying liquid-phase oxidation processes over a solid catalyst relate to (1) the stability of the catalyst to leaching of the active component and to other transformations, (2) the true heterogeneity of the oxidation catalysis, and (3) the possibility of catalyst recycling. Previously, the stability of Co-POM/silica composite material was demonstrated in IBA oxidation with molecular oxygen [61].

In this work, we revealed that the supported Co-POM catalysts do not lose their activity/selectivity during at least 5 catalytic cycles of α-pinene autoxidation (Fig. 4). At the same time, in the case of α-pinene and IBA co-oxidation, the catalyst activity remains constant for a few catalytic cycles and then decreases (Fig. 5). The most plausible explanation for the loss of catalyst activity is the formation of carboxylic acid, which can destroy the structure of Co-POM or matrix or can bind to active cobalt centers. Isobutyric acid also may induce some leaching of Co-POM from the solid matrix. We have checked the amount of cobalt on the support before and after treatment with isobutyric acid (0.3 M in MeCN, 25 °C, 1 h) by elemental analysis and found that the cobalt content was reduced 1.9 times.

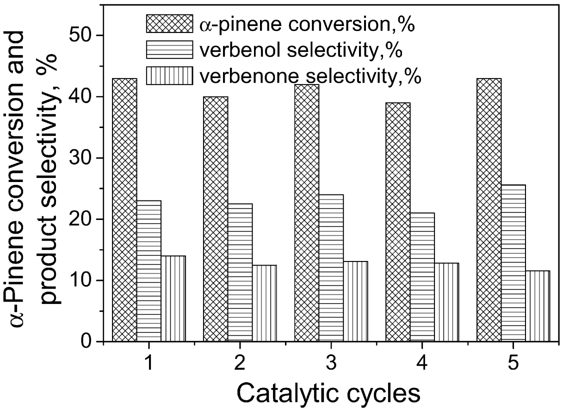


Fig. 4. Catalyst recycling in α-pinene autoxidation over Co-POM/NH_2-MCF. For the reaction conditions, see Section 2 (treatment A).

According to the FTIR data, the Co-POM structure is retained during α-pinene oxidation (Fig. 1). The nitrogen adsorption data indicate the stability of the porous structure (Table 2). Thus, the loss of activity is most likely due to adsorption of isobutyric acid on the catalyst surface and its binding to Co-POM. Indeed, DRS–UV–vis studies pointed out some changes in the position and intensity of *d–d* transition bands after α-pinene/IBA co-oxidation, most likely due to partial substitution of water molecules for isobutyric acid in the coordination sphere of cobalt(II) (Fig. 2). Similar changes were seen when H_2O was replaced by MeCN in $PW_{11}Co(H_2O)O_{39}^{5-}$ [61]. Previously, the formation of complexes between Co-POM and isobutyric acid was revealed and quantitatively studied by ^{31}P NMR [61]. In fact, catalyst regeneration appeared to be possible by evacuation at elevated temperature (Fig. 6).

The experiments with fast catalyst filtration performed at the reaction temperature showed that α-pinene conversion in the filtrate stopped after removal of the catalyst in the case of α-pinene autoxidation (Fig. 7a). This finding supports the heterogeneous nature of the oxidation catalysis. In contrast, in the case of α-pinene and IBA co-oxidation, further α-pinene transformation occurs in the filtrate after catalyst removal, yet the reaction rate is higher than that in the blank experiment (Fig. 7b). This indicates that Co-POM leaching from the solid matrix into the solution occurs and that catalysis has at least a partially homogeneous nature. The experiments with fast catalyst filtration are in good agreement with the elemental analysis data (Table 1), which unambiguously show that some leaching of Co-POM occurs during α-pinene/IBA co-oxidation. Note that the degree of leaching decreases in the following order: xerogel > SBA-15 > MCF (Table 1). Interestingly, the activity of Co-POM/NH_2-MCF is maintained despite the leaching

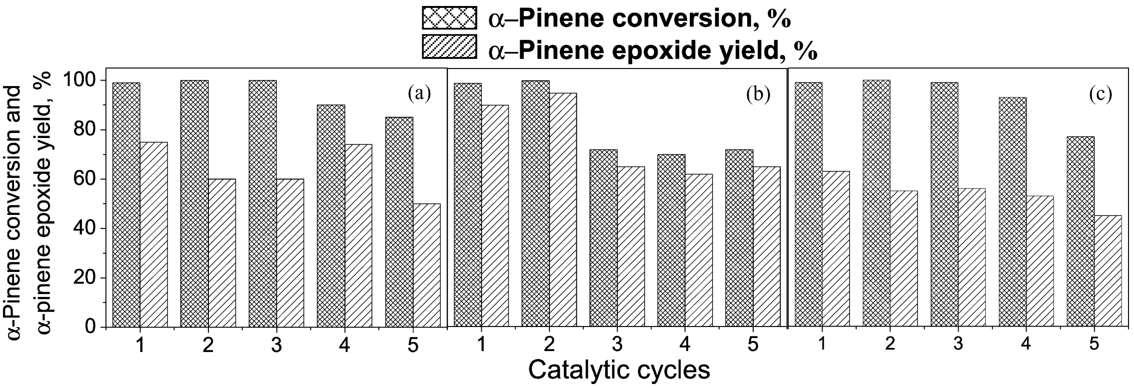


Fig. 5. Catalyst recycling in α-pinene co-oxidation with IBA: (a) Co-POM/NH_2-SBA-15, (b) Co-POM/NH_2-MCF, and (c) Co-POM/NH_2-xerogel. For the reaction conditions, see Section 2 (treatment A).

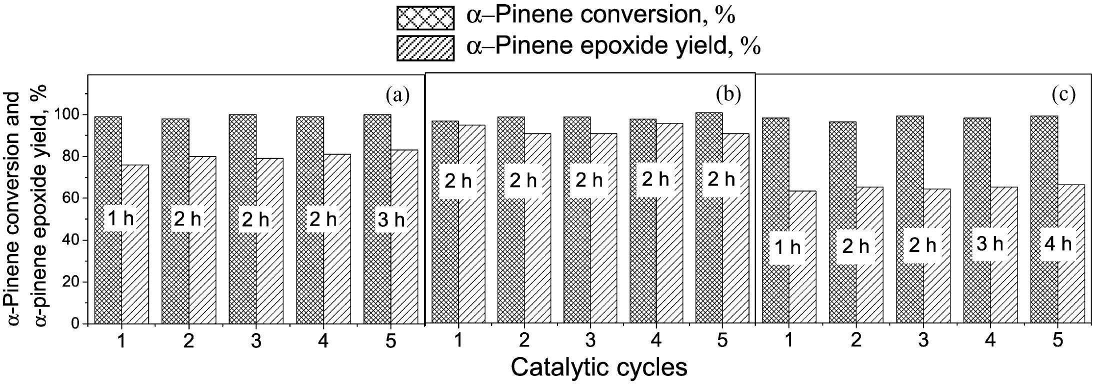
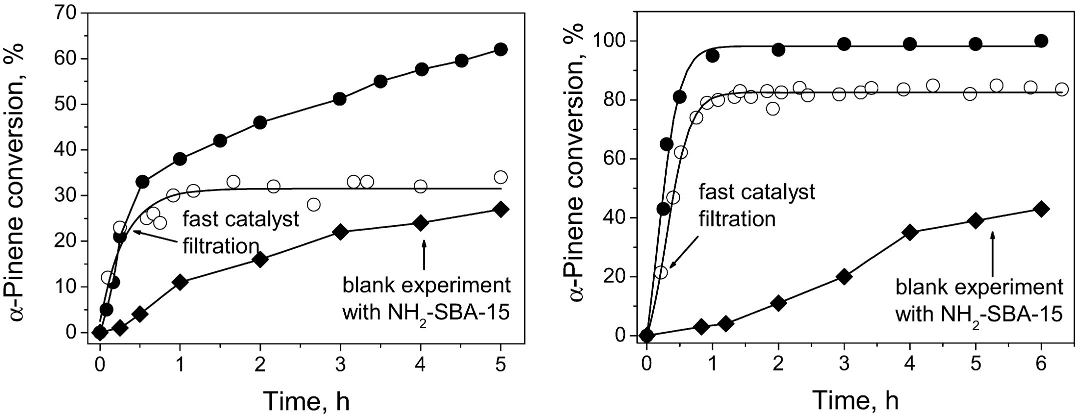


Fig. 6. Recycling regenerated catalyst in α-pinene co-oxidation with IBA: (a) Co-POM/NH_2-SBA-15, (b) Co-POM/NH_2-MCF, and (c) Co-POM/NH_2-xerogel. For the reaction and catalyst regeneration conditions, see Section 2 (treatment B).



(a) (b)

Fig. 7. (a) α-Pinene autoxidation and (b) α-pinene co-oxidation with IBA over Co-POM/NH_2-SBA-15. For the reaction conditions, see Section 2.

(Fig. 6). This may be due to a bell-shaped dependence of the oxidation rate versus catalyst concentration that is well known for Co-containing catalysts [68–70]. Consequently, the catalyst activity is maintained over a rather wide range of catalyst concentrations.

4. Conclusion

The Co-containing polyoxometalate $[Bu_4N]_4H[PW_{11}Co(H_2O)O_{39}]$ was electrostatically bound to various NH_2-modified silica matrixes, including SiO_2-xerogels, MCF, and SBA-15. The retention of the Co-POM structure on immobilization and after catalytic runs was demonstrated by FTIR and DRS–UV–vis. It was found that α-pinene autoxidation in the presence of the supported Co-POM catalysts leads to formation of the allylic oxidation products verbenol and verbenone, with selectivity in the range of 60–70% at about 20% conversion. At higher conversion, the selectivity decreases due to overoxidation. α-Pinene co-oxidation with isobutyraldehyde selectively affords α-pinene epoxide, with the selectivity depending on the amount of NH_2 groups on the support and attaining 94% at 96% alkene conversion.

The catalysis of α-pinene autoxidation over the electrostatically immobilized Co-POM most likely has a true heterogeneous nature. In this process, the supported Co-POM catalysts can be recycled without suffering a loss in activity/selectivity. In contrast, homogeneous catalysis contributes significantly to α-pinene/IBA co-oxidation due to the leaching of the active Co-POM into solution. The degree of leaching depends on the nature of the silicate matrix and reduces in the following order: Co-POM/NH_2-xerogel > Co-POM/NH_2-SBA-15 > Co-POM/NH_2-MCF. The activity remains constant over several catalytic cycles when catalyst regeneration via evacuation is performed to remove adsorbed carboxylic acid.

Acknowledgments

This research was partially supported by the Russian Foundation for Basic Research (RFBR-CNRS Grant 05-03-34760) and the CRDF (award NO-008-X1 to N.V.M.). The authors thank V. Utkin and A. Tkachev for the product identification by GC/MS and T. Larina for the DRS–UV measurements.

References

[1] W.F. Erman, Chemistry of the Monoterpenes: An Encyclopedic Handbook, Dekker, New York, 1985.
[2] K. Bauer, D. Garbe, H. Surburg, Common Fragrance and Flavor Materials, Wiley–VCH, New York, 1997.
[3] C. Mercier, P. Chabardes, Pure Appl. Chem. 66 (1994) 1509.
[4] P.Z. Bedoukian, Am. Perf. Cosm. 86 (1971) 25.

[5] P.A. Wender, T.P. Mucciaro, J. Am. Chem. Soc. 114 (1992) 5878.
[6] J.B. Lewis, G.W. Hedrick, J. Org. Chem. 30 (1965) 4271.
[7] M. Albert, S.G. Traynor, R.L. Webb, in: D.E. Zinkel, J. Russel (Eds.), Nacal Stores, PULP Chemical Association, New York, 1989, p. 479.
[8] R.N. Moore, C. Golumbic, G.S. Fisher, J. Am. Chem. Soc. 78 (1956) 1173.
[9] US Patent 2 911 442 (1959) to The Glidden Company.
[10] GB Patent 761 656 (1956) to The Glidden Company.
[11] N. Fdil, A. Romene, S. Allaoud, A. Karim, Y. Castanet, A. Morteux, J. Mol. Catal. A Chem. 108 (1996) 15.
[12] T. Joseph, D.P. Sawant, C.S. Gopinath, S.B. Halligudi, J. Mol. Catal. A Chem. 184 (2002) 289.
[13] R. Chakrabarty, B.K. Das, J. Mol. Catal. A Chem. 223 (2004) 39.
[14] M.M. Reddy, T. Punniyamurthy, J. Iqbal, Tetrahedron Lett. 36 (1995) 159.
[15] M.J. da Silva, P. Robles-Dutenhefner, L. Menini, E.V. Gusevskaya, J. Mol. Catal. A Chem. 201 (2003) 71.
[16] M. Lajunen, A.M.P. Koskinen, Tetrahedron Lett. 35 (1994) 4461.
[17] M. Lajunen, T. Maunula, A.M.P. Koskinen, Tetrahedron 56 (2000) 8167.
[18] M. Lajunen, M. Myllykoski, J. Asikkala, J. Mol. Catal. A Chem. 198 (2003) 223.
[19] G. Rothenberg, Y. Yatziv, Y. Sasson, Tetrahedron 54 (1998) 593.
[20] C.-C. Guo, W.-J. Yang, Y.-L. Mao, J. Mol. Catal. A Chem. 226 (2005) 279.
[21] P. Robles-Dutenhefner, M.J. da Silva, L.S. Sales, E.M.B. Sousa, E.V. Gusevskaya, J. Mol. Catal. A Chem. 217 (2004) 139.
[22] T. Yamada, T. Takai, O. Rhode, T. Mukajama, Bull. Chem. Soc. Jpn. 64 (1991) 2513.
[23] T. Takai, E. Hata, T. Yamada, T. Mukajama, Bull. Chem. Soc. Jpn. 64 (1991) 2109.
[24] T. Yamada, K. Imagawa, T. Mukajama, Chem. Lett. (1992) 2109.
[25] T. Takai, E. Hata, K. Yorozu, T. Mukajama, Chem. Lett. (1992) 2077.
[26] T. Mukaiyama, K. Yorozu, T. Takai, T. Yamada, Chem. Lett. (1993) 439.
[27] J. Iqbal, S. Bhatia, M. Reddy, Synth. Commun. 23 (1993) 2285.
[28] M. Hamamoto, K. Nakayama, Y. Nishiyama, Y. Ishii, J. Org. Chem. 58 (1993) 6421.
[29] N. Mizumo, T. Hirose, M. Tateshi, M. Iwamoto, Chem. Lett. (1993) 1839.
[30] N. Mizumo, M. Tateshi, T. Hirose, M. Iwamoto, Chem. Lett. (1993) 1985.
[31] M. Hamamoto, K. Nakayama, Y. Nishiyama, Y. Ishii, J. Org. Chem. 58 (1993) 6421.
[32] N. Mizumo, T. Hirose, M. Tateshi, M. Iwamoto, Stud. Surf. Sci. Catal. 82 (1994) 593.
[33] K. Yorozu, T. Takai, T. Yamada, T. Mukajama, Bull. Chem. Soc. Jpn. 67 (1994) 2195.
[34] N. Mizuno, T. Hirose, M. Iwamoto, in: V.C. Corberan, S.V. Bellon (Eds.), New Developments in Selective Oxidation II, Elsevier, Amsterdam, 1994, p. 593.
[35] N. Mizuno, T. Hirose, M. Tateishi, M. Iwamoto, J. Mol. Catal. 88 (1994) L125.
[36] A.M. Khenkin, A. Rosenberg, R. Neumann, J. Catal. 182 (1999) 82.
[37] O.A. Kholdeeva, V.A. Grigoriev, G.M. Maksimov, M.A. Fedotov, A.V. Golovin, K.I. Zamaraev, J. Mol. Catal. A Chem. 114 (1996) 123.
[38] O.A. Kholdeeva, I.V. Khavrutskii, V.N. Romannikov, A.V. Tkachev, K.I. Zamaraev, Stud. Surf. Sci. Catal. 110 (1997) 947.
[39] O.A. Kholdeeva, V.N. Romannikov, A.V. Tkachev, I.V. Khavrutskii, K.I. Zamaraev, Stud. Surf. Sci. Catal. 108 (1997) 337.
[40] M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer, Berlin, 1983.
[41] J.B. Moffat, Metal-Oxygen Clusters: The Surface and Catalytic Properties of Heteropoly Oxometalates, Kluwer/Plenum, New York, 2001.
[42] C.L. Hill, C.M. Prosser-McCartha, Coord. Chem. Rev. 143 (1995) 407.
[43] N. Mizuno, M. Misino, Chem. Rev. 98 (1998) 199.
[44] R. Neumann, Prog. Inorg. Chem. 47 (1998) 317.
[45] J.E. Lyons, P.E. Ellis, V.A. Durante, Stud. Surf. Sci. Catal. 67 (1991) 99.
[46] N. Mizuno, M. Tateishi, T. Hirose, M. Iwamoto, Chem. Lett. (1993) 2137.
[47] N. Mizuno, T. Hirose, M. Iwamoto, J. Mol. Catal. 88 (1994) L125.
[48] H. Weiner, R.G. Finke, J. Am. Chem. Soc. 121 (1999) 9831.
[49] R. Neumann, M. Fahan, J. Chem. Soc. Chem. Commun. (1995) 2277.
[50] Y. Izumi, Res. Chem. Intermed. 24 (1998) 461.
[51] A.M. Khenkin, R. Neumann, A.B. Sorokin, A. Tuel, Catal. Lett. 63 (1999) 189.
[52] L. Xu, E. Boring, C.L. Hill, J. Catal. 195 (2000) 394.
[53] A.N. Kharat, P. Pendleton, A. Badalyan, M. Abenini, M.M. Amini, J. Mol. Catal. A Chem. 175 (2001) 277.
[54] W. Kaleta, K. Nowinska, Chem. Commun. (2001) 535.
[55] B.J.S. Johnson, A. Stein, Inorg. Chem. 40 (2001) 801.
[56] R. Neumann, M. Levin, J. Org. Chem. 56 (1991) 5707.
[57] S. Fujibayashi, K. Nakayama, M. Hamamoto, S. Sakaguchi, Y. Nishiyama, Y. Ishii, J. Mol. Catal. A 110 (1996) 105.
[58] K. Nakayama, M. Hamamoto, Y. Nishiyama, Y. Ishii, Chem. Lett. (1993) 1699.
[59] N.M. Okun, T.M. Anderson, C.L. Hill, J. Am. Chem. Soc. 125 (2003) 3194.
[60] N.M. Okun, T.M. Anderson, C.L. Hill, J. Mol. Catal. A 197 (2003) 283.
[61] O.A. Kholdeeva, M.P. Vanina, M.N. Timofeeva, R.I. Maksimovskaya, T.A. Trubitsina, M.S. Melgunov, E.B. Burgina, J. Mrowiec-Bialon, A.B. Jarzebski, C.L. Hill, J. Catal. 226 (2004) 363.
[62] M.S. Mel'gunov, E.A. Mel'gunova, A.N. Shmakov, V.I. Zaikovskii, Stud. Surf. Sci. Catal. 146 (2003) 543.
[63] X.S. Zhao, G.Q. Lu, X. Hu, Chem. Commun. (1999) 1391.
[64] T.J.R. Weakley, S.A. Malik, J. Inorg. Nucl. Chem. 29 (1967) 2935.
[65] N.V. Maksimchuk, M.S. Melgunov, J. Mrowiec-Białoń, A.B. Jarzębski, O.A. Kholdeeva, J. Catal. 235 (2005) 175.
[66] T.J.R. Weakley, J. Chem. Soc. Dalton Trans. (1973) 341.
[67] J.E. Ancel, N.V. Maksimchuk, I.L. Simakova, V.A. Semikolenov, Appl. Catal. A Gen. 272 (2004) 109.
[68] F. Marta, E. Boga, M. Matok, Discuss. Faraday Soc. (1968) 173.
[69] O.A. Kholdeeva, V.A. Grigoriev, G.M. Maksimov, K.I. Zamaraev, Top. Catal. 3 (1996) 313.
[70] O.A. Kholdeeva, V.A. Grigoriev, G.M. Maksimov, M.A. Fedotov, A.V. Golovin, K.I. Zamaraev, J. Mol. Catal. A Chem. 114 (1996) 123.