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

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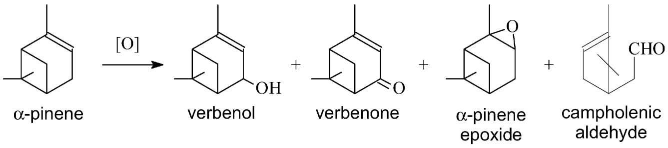
Abstract

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 [$100\,^\circ C/30$ atm O_2 for Co(II)Saloph-Y and $60\,^\circ C/10$ 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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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.