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Catalysis Today 107–108 (2005) 230–234
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Application of complex heteropolytungstates in limonene epoxidation by H_2O_2 in biphasic medium

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Abstract

The synthesis of potassium salts of Cu heteropolytungstate was carried out by reaction in aqueous solution of $Na_8H[\Delta PW_9O_{34}]\cdot 19H_2O$ lacunary precursor with Cu nitrate in KCl excess. The product is a mixture of two isomers related to Keggin structure, having a composition $K_{5.5}Na_{1.5}[PW_{10}O_{38}Cu_2(H_2O)_2]\cdot 13H_2O$, which are the main phases, while the tetra-nuclear copper cluster with formula: $[K_{10}(PW_9O_{34})_2Cu_4(H_2O)_2]\cdot 20H_2O$ was the minority phase. The characterization was carried out by means of X-ray powder diffraction analysis (XRD) and vibrational FT-IR and Raman spectroscopy. The Cu-phase mixture was used as catalyst for the epoxidation of limonene in biphasic (water–organic) reaction media using hydrogen peroxide (35% aqueous H_2O_2) as the oxygen donor. It was able to oxidize selectively limonene towards the epoxide at very high turnover numbers. In addition, similar studies were performed with both the structural related ($[K_{10}(PW_9O_{34})_2Co_4(H_2O)_2]\cdot 20H_2O$) and the lacunary precursor for comparative purposes. Some comments about the stability of copper and cobalt tetra-nuclear phases were made on the basis of topological and electronic considerations and the distortion of the metal environments was related to the catalytic behavior.

Keywords: Heteropolytungstates; Catalytic oxidations; Limonene; Hydrogen peroxide

1. Introduction

The present environmental trends have forced fine chemicals industries to re-evaluate their processes in order to reduce contaminant effluents resulting from stoichiometric oxidation processes. Therefore, it is of great interest to use effective and selective catalytic systems in combination with hydrogen peroxide as oxygen donor (clean oxidant agent) for the oxidation of organic substrates. Also, the terpene-oxygenated derivates are of great interest due to the fact that they are used in the production of fragrances and perfumes [1]. The limonene oxidation in heterogeneous conditions has been reported by Villa et al. [2] using hydrogen peroxide and tungstophosphoric acid anchored in Amberlyst IRA 900. Armendia et al. [3] have also reported the limonene oxidation to limonene oxide using the double layer hydroxides (Mg/Al) in the presence of nitrile. In the same way, Pizzio et al. have used heteropolycompounds containing W or Mo supported on carbon and alumina [4], while Corma et al. used mesoporous materials containing Ti [5] and Crivello et al. used catalysts based on hydrotalcite-type precursors [6].

Venturello et al. have reported homogeneous catalysts based on heteropolyacids working under biphasic conditions as a feasible method for epoxidation of olefins [7,8].

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0920-5861/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.cattod.2005.07.093

Transition metallic ions have been substituted in lacunary polyoxotungstates giving place to polyoxometalates of general formula $[WMM'_2(XW_9O_{34})_2]^{12-}$ where M and M′ are manganese, cobalt, iron, zinc, nickel or copper and X might be zinc or cobalt. These compounds result in the formation of active complexes in reactions of catalytic oxidation of alkenes and alcohols [9,10]. These can be seen as a transition metals coordinated to an inorganic bond which is oxidatively stable.

In order to obtain selectively 1,2-epoxilimonene, the study was carried out by using heteropolymetalates of potential catalytic interest but with a certain structural complexity, i.e., bimetallic complexes constituted by a mixture of Cu isomers related to Keggin structure and a ‘‘sandwich’’-type structure with fragments $[PW_9O_{34}]^{9-}$ [11] linked through a group or ‘‘cluster’’ of metallic ions, resulting in a general formula $[(PW_9O_{34})_2M_4(H_2O)_2]^{10-}$ with M = Cu(II) and Co(II) [12].

The aim of this work was the study of the catalytic reaction for the selective limonene epoxidation in a biphasic system using H_2O_2 (35%, w/w) as clean oxidant, dicloroethane as solvent and the Cu phase above mentioned as the catalyst. Likewise, both the precursor of such phases ($Na_8H[\Delta PW_9O_{34}]\cdot 19H_2O$) and the corresponding Co_4-phase were studied for comparative purposes.

2. Experimental

2.1. Synthesis of catalysts

The precursor $Na_8H[\Delta PW_9O_{34}]\cdot 19H_2O$ was synthesized from stoichiometric amounts of $Na_2WO_4\cdot 2H_2O$, phosphoric acid and acetic acid. The precipitate was treated at 80 °C for 3 days. In order to obtain the catalyst, an aqueous solution of $Cu(NO_3)_2$ was used and the precursor was added at stoichiometric amount and finally an excess of potassic salt. The solution was centrifuged and it was kept at room temperature until the precipitation of crystals occurred, and these were air-dried. The synthesis of Co derivate was carried out in a similar way by using the corresponding nitrate [13]. The catalysts obtained in this way were characterized by different techniques.

2.2. Catalyst characterization

The X-ray powder diffraction patterns obtained for pure samples were registered in a Philips-PW 1729 equipment. Cu Kα radiation (Ni filtered) was used and the register was carried out with a scanning angle between 5° and 60° at a rate of 2θ per minute.

The FT-IR spectra were obtained by using a Bruker IFSS 66 FT-IR equipment (KBr pellet technique). The number of scans was 128 and the resolution was $0.5\ cm^{-1}$.

The Raman spectra were recorded in the range of 200–1600 cm^{-1} with a Raman LabRAM Infinity microprobe (Jobin Yvon) equipped with a liquid nitrogen cooled detector and a frequency-doubled Nd:YAG laser supplying the excitation line at 532 nm. The power at the sample was below 5 mW, the resolution was $3\ cm^{-1}$ and the number scans was 10.

2.3. Catalytic reaction

The stock solution of the catalysts under study was prepared by dissolving: 0.016 mmol of polyoxometalate salt and 0.13 mmol of metiltricaprilamonium chloride (Aliquat 336) in a mixture of the same proportion H_2O/1,2-dichloroethane (5 ml, ratio 1:1). In order that the catalyst could be solubilized in the organic phase, the mixture was stirred and low heating during periods of about 1 h being evident a decolouration of the aqueous phase. Subsequently, the organic phase was separated and cooled.

The oxidation reaction was carried out in a batch-type reactor at atmospheric pressure, under vigorous stirring (800–1000 rpm) and keeping the system at 2 °C during a period of 40 h. In a typical reaction, 3.04 mmol of limonene (L) and the required amount of stock solution were dissolved in 3 ml of 1,2-dicloroethane. The reaction starts by adding peroxide 35% (w/w) (6.08 mmol), forming a biphasic system. The progression of the reaction was followed up by taking small aliquots of the organic phase and these were analysed by gaseous chromatography in a cross-linked methyl capillar column (Silicone Gum, 30 m × 0.53 mm × 2.65 μm film thickness). The reaction products were analysed by comparison with chromatographic witnesses and by GC–mass in a Shimadzu GCMS-QP 5050A.

3. Results and discussion

3.1. Structural and spectroscopic behavior

The complex $[PW_9O_{34})_2M_4(H_2O)_2]^{10-}$ heteropolioxotungstates with M = Co (d^7), Zn (d^{10}) and Mn (d^5) divalent cations can be structurally derived from the union of two $[PW_9O_{34}]^{9-}$ fragments by means of a MO_6 tetra-nuclear cluster, giving rise to the sandwich-type structure (shown in Fig. 1) [12]. The metallic cluster, where the MO_6 groups are linked by the edges, is connected by the corners to the WO_6 and PO_4 groups of two $[PW_9O_{34}]^{9-}$ decapped Keggin phases. The disposition resembles that observed in the 2:1 laminar aluminosilicates, where a brucite-like structure is intercalated between the negative $[(Si,Al)O_4]_n$ layers [14]. Like these species, the sizes of the divalent metallic anions that allow the formation of the W-condensed structure are smaller than 0.83 Å (octahedral coordination). Although the size and charge of the copper species (0.73 Å) are adequate to adopt this structural distribution, the Cu(II) electronic configuration (d^9) hindered the formation of a shared edge octahedral cluster. In fact, the Jahn-Teller effect [15] is responsible for the CuO_6 polyhedral distortion. So, from the topological point of