Catalytic Epoxidation of Olefins by Nanolayered Polyoxomolydate [4,4´-H2bipy][Mo7O22].(H2O)

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Abstract

A two-dimensional nanolayered polyoxomolydate, [4,4´-H2bipy][Mo7O22].H2O (1), where 4,4´-bipy = 4,4´-bipyridine, was prepared and characterized by FT-IR and atomic absorption spectrosopies, transmission electron microscopy (TEM), X-ray single crystal and powder diffraction (XRD), and thermogravimetric analysis. The catalytic performance of 1 was assessed in the epoxidation of some olefins employing tert-butyl hydroperoxide (TBHP) as oxidant and acetonitrile as solvent. Compound 1 showed moderate to excellent activity and selectivity towards the epoxidation of the olefins. Thermal, structural and catalytic stability of 1 as well as its reusability were examined. The effect of the catalyst amount and the nature of solvent on the activity of 1 were also investigated.

Keywords: Nanolayered; Polyoxomolydate; 4,4´-bipyridine; Epoxidation catalyst.

Introduction

Catalytic oxidation of olefins is attractive from industrial point of view due to the production of various chemical intermediates such as epoxides, ketones and allylic alcohols depending on certain reaction conditions [1].

Polyoxometalate (POM) clusters, notably those containing Mo and W, have been shown to be promising catalysts for the oxidation of olefins [2,3]. Polyoxomolydates such as (bmim)[PMo12O40] (bmim = 1-butyl-3-methylimidazolium tetrafluoroborate) [4], \{(NH4)2[Mo12Mo11O372(CH3COO)30(H2O)72] \} [5] and H3PMo12-nWnO40 (n = 1-11) [6] were designed and applied for the oxidation of olefins.

The development of heterogeneous and easily recyclable catalysts is the challenging aim of liquid phase oxidation catalysis [7]. Many research groups have made attempts to prepare POM-based heterogeneous catalysts using immobilization techniques [8-13]. In this regard, different approaches like grafting of POM on NH2-modified mesoporous silica [14], embedding POM in a silica matrix [15] and incorporation of POM within nanocages of the coordination polymer MIL-101 [16] have been reported.

Inorganic-organic hybrid materials containing catalytically active POM can behave as heterogeneous catalysts in the epoxidation of olefins [17]. The two-dimensional molybdenum (VI) polymer

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CH2Cl2 according to a previously reported method [22]. Prepared from commercial aqueous 70% TBHP using used as received. Anhydrous TBHP solution was placed at idealized positions and refined as riding. The structure of compound 1 (70 mg) in CH3CN (5 ml) in a round-bottom flask. After addition of TBHP (30 mmol), the reaction mixture was refluxed for 14 hours. The solid was filtered and washed with fresh acetonitrile. The filtrate was analysed by GC and GC-MS.

Materials and Methods

All chemicals were of commercial reagent grade and as received. Anhydrous TBHP solution was prepared from commercial aqueous 70% TBHP using CH3Cl2 according to a previously reported method [22].

In this paper, we report the catalytic activity of compound 1 in the epoxidation of some olefins. This two-dimensional catalyst is insoluble in many kinds of solvents due to the presence of extensive interactions in the network. Therefore the catalyst was used in the liquid-phase olefin epoxidation and the details of activity, selectivity, stability and reusability of the catalyst were investigated.

Catalytic epoxidation of olefins

The desired olefin (10 mmol) was added to a mixture of compound 1 (70 mg) in CH3CN (5 ml) in a round-bottom flask. After addition of TBHP (30 mmol), the reaction mixture was refluxed for 14 hours. The solid was filtered and washed with fresh acetonitrile. The filtrate was analysed by GC and GC-MS.

Results and Discussion

The colorless crystals of 1 were prepared under hydrothermal condition with controlled pH value and then applied as a catalyst for the oxidation of some olefins. Surprisingly, single-crystal X-ray analysis of the catalyst revealed that the structure was previously reported by Zapfa [19] although we changed the reaction time and replaced the initial reactants of MoO3 and Mo (250 mesh) with (NH4)6Mo7O24.4H2O. We also used Co(NO3)2.6H2O (0.087 g, 0.3 mmol), 4,4'-bipyridine (0.02 g, 0.1 mmol), HNO3 (1 ml, 1 M) and H2O (15 ml) was stirred for 15 minutes in air (pH = 3.5) and then placed in a 23 ml Teflon-lined stainless steel autoclave. The autoclave was sealed, heated at 200 °C for 3 days and then cooled to room temperature at the rate of 10 °C h⁻¹. The colorless crystals were filtered, washed with distilled water and dried in air.

The metal content of the catalyst was determined using GBC atomic absorption spectrometer. Oxidation products were analyzed using a gas chromatograph (HP, Agilent 7890) equipped with a capillary column (HP-5) and FID detector. GC-MS of the products was recorded using 7890-5975C with a capillary column HP-DHA7.

Synthesis of [4,4'-H2bipy][MoO2:7H2O (1)]

A mixture of (NH4)6MoO24.4H2O (0.124 g, 0.1 mmol), Co(NO3)2.6H2O (0.087 g, 0.3 mmol), 4,4'-bipyridine (0.02 g, 0.1 mmol), HNO3 (1 ml, 1 M) and H2O (15 ml) was stirred for 15 minutes in air (pH = 3.5) and then placed in a 23 ml Teflon-lined stainless steel autoclave. The autoclave was sealed, heated at 200 °C for 3 days and then cooled to room temperature at the rate of 10 °C h⁻¹. The colorless crystals were filtered, washed with distilled water and dried in air.

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The catalyst contains [MoO2:22]22⁻ layers constructed from edge- and corner-sharing {MoO6} octahedra. The water molecules and the bipyridinium cations occupy the interlamellar space among the layers to form the two-dimensional nanolayered structure of 1. High resolution TEM image of the catalyst is shown in Figure 1b. The image confirms the nanolayered structure of 1 and reveals that the distance between parallel sheets of molybdenum oxide is about 1 nm that is in agreements
Similarity of the XRD pattern of the fresh catalyst (Figure 2b) and the simulated pattern obtained from single crystal data (Figure 2a) confirms the phase purity of the prepared crystals. The intensity differences in the patterns seem to be due to the preferred orientation of the powdered sample.

Thermogravimetric study of the catalyst was performed under argon atmosphere in the temperature range of 25-600 °C. As presented in Figure 3, TGA analysis of the catalyst shows no weight loss up to 385 °C. The catalyst decomposes in the temperature range of 385-530 °C in two steps. The first weight loss (13.6 %) in the 385-400 °C corresponds to the release of 4,4´-bipy ligand (calculated 13 %). The second weight loss (3.6 %) at about 500 °C can be due to the release of two water molecules (calculated 3 %) and the remaining product is ascribed to 7 MoO₃ (found 82.8%, calculated 83.9%). The XRD analysis of the remaining product also confirms that the residual is MoO₃ (Figure 4).

It has been reported that polyoxomolybdates are able to catalyze olefin oxidation with H₂O₂ [18, 26-27]. Herein, we employed TBHP as oxidant instead and investigated the catalytic activity of the prepared catalyst in the epoxidation of some olefins. Cyclohexene was selected as the representative substrate for further investigation of the reaction conditions (i.e. reaction time, catalyst amount and solvent). Figure 5 illustrates the results obtained for the oxidation of cyclohexene in the presence of compound 1 as a catalyst within various reaction times. The more reaction time results in the higher conversion of cyclohexene.

The effect of the amount of catalyst and the nature of solvent on the oxidation of cyclohexene is presented in Table 1. The reaction conversion is improved by increasing the amount of catalyst.

Moreover, the nature of solvent is very important in the catalytic reactions performed in the liquid phase [28, 29]. As shown in Table 1, the oxidation reaction proceeded better in CH₃CN. Apparently tetrahydrofuran (THF) as a solvent with more coordination ability displayed poor activity in the reaction due to its competition with TBHP to occupy the coordination sites of the molybdenum catalyst. Therefore epoxidation reactions of the other olefins were performed in CH₃CN.
as solvent and the results are summarized in Table 2.

Stability of compound 1 under reaction conditions was examined by catalyst recycle-recovery experiments for three runs using cyclohexene as a model substrate. The results (Table 1) indicate that the conversion decreased from 78 to 75 % and 62 to 50 % after reusing the catalyst due to small amount of molybdenum leaching. Molybdenum content of the fresh and reused catalyst was determined using atomic absorption spectroscopy. The molybdenum content of the recovered catalyst was shown to be 50.62 % with little change of 0.63 % compared to that of fresh catalyst (51.25 %). ICP determination of the filtrate showed that the amount of molybdenum ions was 0.64 % indicating that compound 1 could be considered as a low leaching heterogeneous catalyst. The reaction was allowed to continue after filtration of the catalyst and no further changes were observed in the conversion after 4 h.

FT-IR spectra of the fresh and recovered catalyst are similar and exhibited in Figure 6. The strong band appeared at 908 cm⁻¹ is attributed to $\nu$(Mo=O). The bands displaying at 790-850 cm⁻¹ are related to $\nu$(Mo-
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A group of bands located at the 1200-1630 cm⁻¹ region is corresponded to the 4,4´-bipyridine ligand [25, 30].

The XRD patterns of the fresh and recovered catalyst are depicted in Figure 2. The similarity of the patterns clearly indicates that the crystalline structure of compound 1 has retained after using the catalyst for the epoxidation reactions.

The feasible mechanism for the epoxidation of the olefins with TBHP in the presence of compound 1 is depicted in Scheme 1. Based on the reported epoxidation mechanisms [31-33], epoxide formation involves the coordination of the oxidant to Mo (VI) center and the attack of the olefin on the Mo (VI)-coordinated t-butyl hydroperoxide.

In conclusion, we have reported the catalytic activity of the prepared nanolayered polyoxomolybdate 1 toward the epoxidation of some olefins, as well as the optimized conditions for the reaction. Compound 1 exhibited good catalytic activity and selectivity in the epoxidation reaction of some olefins with TBHP in acetonitrile. It was also found that the catalyst was stable in the reaction conditions due to extensive hydrogen-bonding interactions in the network formed among bipyridinium cations, lattice water molecules and terminal oxo groups of molybdenum. Therefore the catalyst could be easily separated and reused without decomposition of the network or appreciable desorption.

References


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