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

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Abstract

A two-dimensional nanolayered polyoxomolybdate, [4,4′-H2bipy][Mo7O22].H2O (1), where 4,4′-bipy = 4,4′-bipyridine, was prepared and characterized by FT-IR and atomic absorption spectroscopies, 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; Polyoxomolybdate; 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]. Polyoxomolybdates such as $(bmim)_3[PMo_{12}O_{40}]$ (bmim = 1-butyl-3-methyl-imidazolium tetrafluoroborate) [4], $\{(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}\}$ [5] and $H_3PMo_{12-n}W_nO_{40}$ (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 NH_2-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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[MoO$_2$Cl$_2$(H$_2$O)$_2$].(H$_2$dipy-pra)Cl$_2$ (dipy-pra = 1, 3-bis (4-pyridyl) propane) has been utilized as an efficient catalyst for olefin epoxidation [18]. The synthesis of molybdenum oxide compounds in combination with the structure-directing ability of organo-diamines such as 4,4′-bipy can lead to the formation of polyoxomolybdate networks. A series of polyoxomolybdates based on 4,4′-bipy have been synthesized such as two-dimensional hydrogen-bonded network of [(4,4′-H$_2$bipy) (Mo$_7$O$_{22}$)(H$_2$O)]$_n$ [19], bimetallic polymers of [{Ni(H$_2$O)$_2$(4,4′-bipy)$_2$}$_2$Mo$_8$O$_{26}$ and [{Cu(4,4′-bipy)}$_4$Mo$_{15}$O$_{47}$].8H$_2$O [20] as well as [H$_2$bpy]$_2$[Hbpy][PZnMo$_{11}$O$_{39}$].2.75 H$_2$O [21].

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.

Materials and Methods

All chemicals were of commercial reagent grade and used as received. Anhydrous TBHP solution was prepared from commercial aqueous 70% TBHP using CH$_2$Cl$_2$ according to a previously reported method [22].

FT-IR spectra were recorded on BrukerEnquinox 55 spectrometer equipped with a single reflection diamond ATR system over the range of 600-4000 cm^{-1}. Thermogravimetric analysis (TGA) was carried out under argon atmosphere on a TGA Q50 V6.3 Build 189 instrument at the heating rate of 20 K. min^{-1}. Transmission electron microscopy (TEM) was carried out on a Philips CM30. X-ray powder diffraction (XRD) data were recorded on a Philips PW1800 diffractometer using Cu Kα radiation (λ = 1.5406 Å) ranging from 5° to 50°. The simulated XRD pattern was obtained using the Mercury program for the corresponding single-crystal data. Diffraction data was collected at room temperature on a Bruker APEX-II difractometer using Mo Kα radiation (λ = 0.71073 Å). Cell refinement and data reduction were performed using the algorithms implemented in SAINT Bruker (Bruker AXS Inc. 2007, Madison, Wisconsin, USA). The structure was solved by direct methods using SHELXS-97 and the obtained model refined with SHELXL [23]. All non-hydrogen atoms were refined anisotropically. H atoms were placed at idealized positions and refined as riding. Inductive coupled plasma optical emission spectroscopy (ICP-OES) was carried out with a Varian-MPX instrument. 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′-H$_2$bipy][Mo$_7$O$_{22}$].H$_2$O (1)

A mixture of (NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O (0.124 g, 0.1 mmol), Co(NO$_3$)$_2$.6H$_2$O (0.087 g, 0.3 mmol), 4,4′-bipyridine (0.02 g, 0.1 mmol), HNO$_3$ (1 ml, 1 M) and H$_2$O (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.

Catalytic epoxidation of olefins

The desired olefin (10 mmol) was added to a mixture of compound 1 (70 mg) in CH$_3$CN (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 Discusion

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 MoO$_3$ and Mo (250 mesh) with (NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O. We also used Co(NO$_3$)$_2$.6H$_2$O as one of the precursors, however cobalt ion did not appear in the final product. When the pH value was lower or higher than 3.5, no suitable crystals for single-crystal X-ray diffraction were obtained. The acidic condition of the reaction mixture plays an important role in the assembly of POM-based supramolecules [24, 25]. The structure of compound **1** is presented in Figure 1a.

The catalyst contains [Mo$_7$O$_{22}$]$_n$$^{2n-}$ layers constructed from edge- and corner-sharing {MoO$_6$} 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
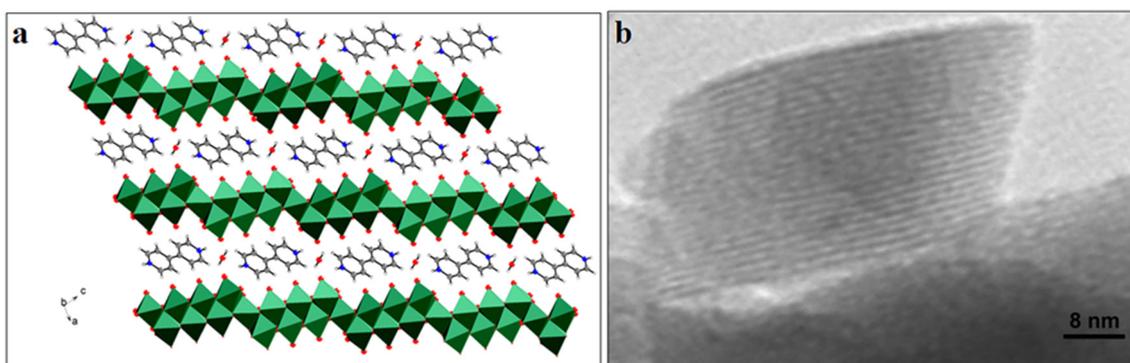
Figure 1. (a) A view of the structure and (b) high resolution TEM image of compound **1**.

with single crystal X-ray data.

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.
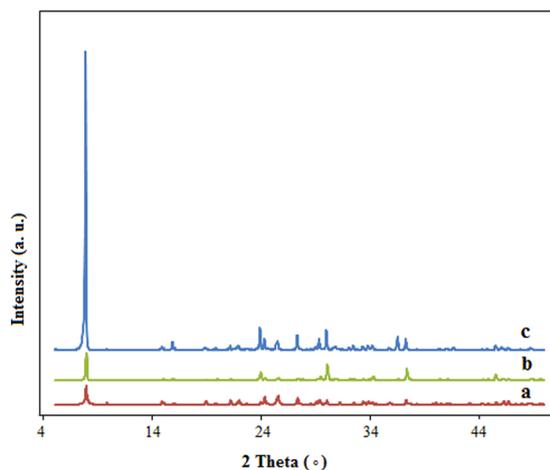
Figure 2. X-ray powder diffraction patterns of compound **1**, (a) simulated from single-crystal data, (b) obtained before and (c) after being used.
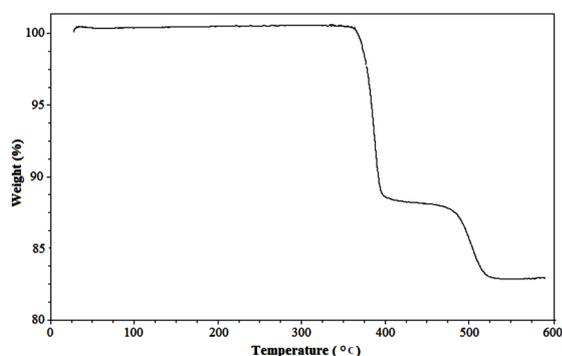
Figure 3. Thermogravimetric curve for compound **1**.

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 MoO_3 (found 82.8%, calculated 83.9%). The XRD analysis of the remaining product also confirms that the residual is MoO_3 (Figure 4).

It has been reported that polyoxomolybdates are able to catalyze olefin oxidation with H_2O_2 [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 CH_3CN. 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 CH_3CN
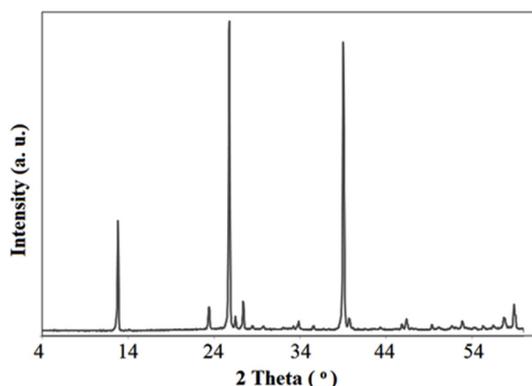
Figure 4. The XRD of compound **1** annealed at 600 °C.
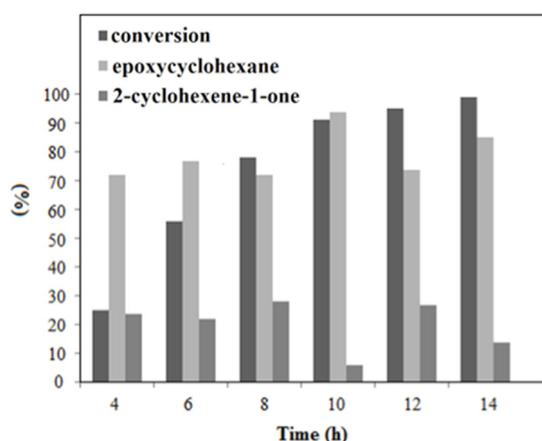
Figure 5. Effect of the reaction time on cyclohexene oxidation. Reaction conditions: cyclohexene (10 mmol), TBHP (30 mmol), CH₃CN (5 ml), catalyst (70 mg).

Figure 6. FT-IR spectra of **1** (a) before and (b) after the reaction.

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 ν (Mo=O). The bands displaying at 790-850 cm⁻¹ are related to ν (Mo-
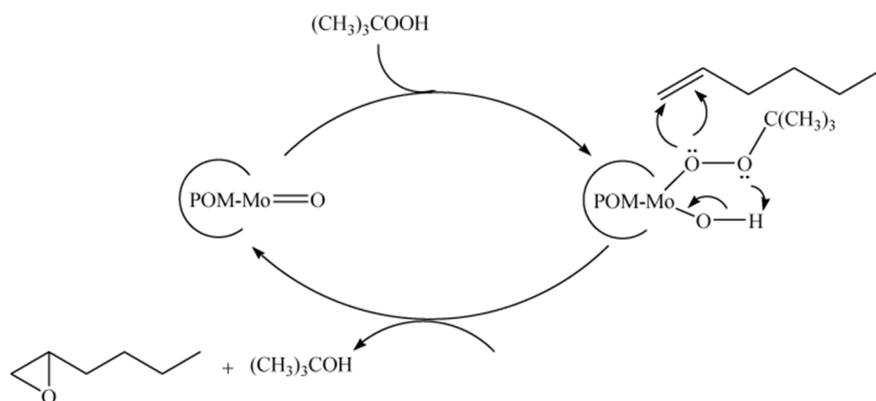
Scheme 1. Proposed mechanism for the epoxidation of 1-hexene in the presence of compound **1**.

Table 1. Influence of the amount of catalyst and its recyclability in the oxidation of cyclohexene.

Entry	Catalyst amount (mg)	Solvent	Time (h)	Conversion (%)	Product selectivity (%)	
					Epoxycyclohexene	2-cyclohexene-1-one
1	30.0	CH$_3$CN	14	21	94	6
2	50.0	CH$_3$CN	14	36	95	5
3	70.0	CH$_3$CN	14	99	85	14
4	70.0	CH$_3$CN	8	78	72	28
5	70.0[a]	CH$_3$CN	8	75	51	49
6	70.0[b]	CH$_3$CN	8	62	58	42
7	70.0[c]	CH$_3$CN	8	50	82	17
8	0.0[d]	CH$_3$CN	5	-	-	-
9	70.0	THF	5	13	53	47
10	70.0	C$_6$H$_5$Cl	5	23	92	6
11	70.0	CH$_3$CN	4	25	72	24

Reaction conditions: cyclohexene (10 mmol), TBHP (30 mmol), solvent (5 ml). [a] 1st cycle; [b] 2nd cycle; [c] 3rd cycle; [d] Without catalyst (in the presence of TBHP)

Table 2. Results of the epoxidation of selected olefins with TBHP in the presence of compound **1**.

Entry	Substrate	Conversion (%)	Selectivity to epoxide (%)	Selectivity to minor products (%)
1	Norbornene	>99	100	0
2	Cyclohexene	>99	85	15[a]
3	*Trans*-stilbene	92	100	0
4	Cyclooctene	>99	100	0
5	1-octene	67	100	0
6	1-hexene	58	100	0

Reaction conditions: substrate (10 mmol), TBHP (30 mmol), catalyst (70 mg), solvent (CH$_3$CN, 5 ml), time (14 h), [a] 2-cyclohexene-1-one

O-Mo). 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.

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