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Synthesis, characterization, and application of a new nanohybrid Schiff base polyoxometalate in epoxidation of olefins in the presence of tert-butyl hydroperoxide

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ABSTRACT

The new molybdenyl acetylacetonate Schiff base complex with mono-lacunary polyoxometalate (**1**) was synthesized in the reaction of $[PMo_{11}O_{39}]^{7}$, molybdenum acetylacetonate $(MoO_2(acac)_2)$, and ethylenediamine. The catalyst was characterized by elemental analysis and various routine techniques like FT-IR, XRD, FESEM, EDX, UV–Vis, and TGA. The catalytic activities of this nanocatalyst were examined for epoxidation of linear, cyclic and phenyl-substituted olefins using tert-butyl hydroperoxide (tert-BuOOH) as oxidant.



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KEYWORDS

Schiff base; polyoxometalate; molybdenylacetylacetonate; olefin epoxidation; nanohybrid; nanocatalyst



1. Introduction

Lacunary Keggin-type polyoxometalates (POMs) are anionic clusters of nanosize transition-metal oxides that display strong coordination with a wide range of organic compounds which leads to formation of new compounds [1–3]. Organic–inorganic hybrid polyoxometalates have been extensively examined [4, 5]. The properties of hybrid materials are the sum of properties of organic and inorganic components [6].

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Physicochemical properties, such as molecular structure, surface charge densities, and strong redox ability [7], make these compounds appropriate for application in magnetism, electronics, electro, and photochromic systems, medicine, molecular batteries, and catalysis [8–11]. Many organic conversions can be catalyzed by POMs due to their redox and acidic properties [12, 13], but due to the good solubility of POMs in polar solvents, it is difficult to isolate the compounds from the reaction mixture [12, 14].

Many reports have been presented on solid catalysts containing metal complexes immobilized on organic or inorganic solid supports as heterogeneous catalysts [15–17], however, slow reaction rates, leaching of the active species, or method of preparation of the complicated catalyst are disadvantages of this method [7]. Hybrid POMs displayed some attractive aspects in contrast to the widely studied supported heterogeneous catalysts. Several catalytic studies have been reported based on these compounds as heterogeneous catalysts with high activity and reusability [12, 18, 19].

Because of the importance of oxidation reactions in industry, many efforts have been made to improve catalytic oxidation systems [20–22]. Epoxidation of alkenes is one of the most important industrial reactions that lead to the preparation of compounds such as surfactants, detergents, lubricating oils, textiles, cosmetics, rubber promoters, epoxy paints, and dyestuff products [23–25].

Dioxomolybdenum(VI) complexes have been shown to be important catalysts or catalyst precursors for oxygen-transfer reactions in chemical and biological systems [26, 27] with many reports on the use of dioxomolybdenum(VI) complexes as catalysts in alkene epoxidation [28–30]. In this article, we synthesized a new nanohybrid Schiff base polyoxometalate by combining the properties of a dioxomolybdenum(VI) complex and a mono lacunary Keggin-type polyoxometalate ($PMo_{11}O_{39}^{-7}$). The synthesized compound was characterized by routine techniques. We have applied **1** as a heterogeneous catalyst for epoxidation of olefins and studied the effect of different solvents, temperatures, oxidant, catalyst, and time on the activity of the catalysts.

2. Experimental

2.1. Instruments and reagents

All solvents and materials were purchased from Merck and Fluka companies and used without purification. $[MoO_2(acac)_2]$ was synthesized from the reported procedure [31] and identified by FT-IR spectroscopy. FT-IR spectra were recorded on a Shimadzu 8400S spectrometer using KBr pellets from 400 to 4000 cm⁻¹. Carbon, hydrogen, and nitrogen elemental analyses were determined on a Perkin-Elmer CHN analyzer. ICP analyses were performed on an ICP-Spectrociros CCD instrument. X-ray powder diffraction (XRD) patterns were obtained by using a Phillips PW-1730 or STOE diffractometer with Cu K α radiation. UV–Vis spectra were recorded on a Perkin-Elmer Lambda 25 spectrophotometer. FESEM equipped by EDS microanalysis was done with a MIRA3TESCAN-XMU instrument. TGA of the sample was carried out using a TA instrument DSC SDT Q600 with a heating rate of 10°C/min under nitrogen. Gas chromatography (GC) was accomplished on a Shimadzu GC-16A instrument using a 2m column packed with silicon DC-200. In the GC experiments, n-decane was used as an internal standard. The operating parameters were as follows: injector temperature, 180°C;



Figure 1. FT-IR spectra of (a) $[MoO_2(acac)_2]$, (b) $[PMo_{11}O_{39}]^{7-}$, and (c) 1.

detector temperature, 200 °C; oven temperature, 70–200 °C. The conversions and yields were calculated by normalizing the areas of the GC peaks by means of the area of the internal standard peak (n-decane).

2.2. Synthesis of mono-lacunary phosphomolybdate molybdenyl acetylacetonato Schiff base

Ethylenediamine (0.05 mL, 0.75 mmol) was added to a stirring solution of 0.456 g (0.25 mmol) of $H_3PMo_{12}O_{40}$ in 15 mL of distilled water. After 30 min, methanol solution of $[MoO_2(acac)_2]$ (0.246 g, 0.75 mmol) was added and the mixture refluxed for 5 h at 80 °C. The light violet precipitate was filtered, washed with methanol, and dried at 80 °C. IR spectrum v, cm⁻¹: 2893 (C-H), 1620 (C = N), 1602 (C = O), 1320 (δ C-H), 1060 (P-O), 946 (Mo = O), 785 and 650 (Mo-O_c-Mo). Found, %: C12.35; H 1.59; Mo 53.38 N 2.31; P 1.34. C₂₄H₃₆Mo₁₃N₄O₄₃P. Calculated, %: C, 12.28; H, 1.53; Mo, 53.16; N, 2.39; P 1.32. M 2347.

2.3. General procedure for the epoxidation of alkenes

All reactions were performed in 10 mL round bottom flasks equipped with a magnetic stir bar and a condenser under reflux. The mixture of alkene (0.5 mmol), catalyst (7 mg,



Figure 2. UV–Vis spectra of (a) [PMo₁₁O₃₉]⁷⁻, (b) [MoO₂(acac)₂], and (c) 1.

3 mmol), and tert-BuOOH (0.4 mL) was refluxed in 1,2-dichloroethane as solvent. The progress of the reaction was monitored by gas chromatographic analysis. Blank experiments were performed in the absence of catalyst under the same experimental conditions. Since different alkenes have various reactivities toward oxidation, the reactions were continued until no further progress was observed.

3. Results and discussion

3.1. Characterization of the nanohybrid catalyst

POMs are unstable in basic media, therefore $[PMo_{12}O_{40}]^{3-}$ changes to mono-lacunary $[PMo_{11}O_{39}]^{7-}$ upon reaction with ethylenediamine. In 2014, Memon and Coworkers reported preparation of a Schiff base in the reaction of acetylacetone and ethylenediamine [32]. The Schiff base complex, **1**, is then obtained in the reaction of molyb-denum acetylacetonate, ethylenediamine, and mono-lacunary POMs as shown in Scheme 1.

Because efforts to obtain suitable crystals for single crystal analysis were unsuccessful, we used the other techniques for characterization of **1**. FT-IR spectra of $[MoO_2(acac)_2]$, $[PMo_{11}O_{39}]^{7-}$, and **1** are compared in Figure 1. Characteristic bands at 2893 (v(C-H)), 1620 (v(C=N)), 1602 (v(C=O)), 1320 (v(C-H)), and 1060 cm⁻¹ (v(P-O_a)) are attributed to formation of **1** [33–35]. Peaks of $[MoO_2(acac)_2]$ and $[PMo_{11}O_{39}]^{7-}$ at 960–860 cm⁻¹ were overlapped.

UV–Vis spectra of $[MoO_2(acac)_2]$, $H_3PMo_{12}O_{40}$, and **1** are shown in Figure 2. The characteristic absorption peak of **1** can be seen at 318 nm which is attributed to O $(p\pi) \rightarrow Mo (d\pi)$ charge transfer transition. This peak is displaced to higher wavelengths than the observed peak (271 nm) in $[MoO_2(acac)_2]$ [36]. The presence of mono-lacunary POM is established by a peak at 214 nm which is attributed to O \rightarrow Mo charge-transfer band [37]. This result confirms an intramolecular interaction between $[MoO_2(acac)_2]$ and POM in **1**.

The XRD patterns of Keggin-type polyoxoanions show two typical refluxing areas $(2\theta = 2-10^{\circ} \text{ and } 25-35^{\circ})$ [38]. The XRD patterns of **1** (Figure 3) show the existence of



Figure 3. XRD pattern of (a) $PMo_{11}O_{39}^{7-}$, (b) $[MoO_2(acac)_2]$, and (c) 1.



Figure 4. FE-SEM images of 1 nanocatalyst.

polyoxometalate and $[MoO_2(acac)_2]$ in this compound. According to these data, **1** has crystalline characteristics after metal loading. By using the Williamson–Hall equation ($\beta \cos \theta = K\lambda/D + 4\varepsilon \sin \theta$, β is line broadening at half of the maximum intensity, K is a dimensionless shape factor (0.9), θ is the Bragg angle, λ is the X-ray wavelength for Cu K α radiation, D is the average crystallite size, and ε is the lattice strain), the average size of the particles was estimated to be 50 nm [39].

FE-SEM is used to examine three important factors: surface crystallography (i.e. the surface formation of atoms), surface morphology (surface structural features based on shape and size), and surface composition (the composition of surface, in terms of elements and compounds). The morphology of **1** is shown in the FE-SEM images (Figure 4). These images show row-like and spherical shapes in **1** with particle sizes of 75–100 and 42–46 nm, respectively, which is in agreement with XRD results. There are slight differences between the particle sizes obtained from FE-SEM and XRD techniques because XRD provides information of the volume and SEM of the surface. Therefore we have a mixture of particles of various sizes.

The EDX spectrum of **1** indicates the existence of C, N, O, P, and Mo elements (Figure 5). These results can be confirmed in the proposed structure of **1**.



Figure 5. EDX spectra of 1.



Figure 6. TGA analysis of 1.

The DTG–TGA curve of **1** shows three main weight losses at 200–280 °C, 300–500 °C, and 650–1000 °C (Figure 6). These weight losses correspond to the removal of imine groups in the Schiff base (267.3 °C, 5.62%), decomposition of molyb-denum acetylacetonate (in two steps) (403.6 and 454.9 °C, 8.59%), and molybdophosphate to P_2O_5 and MoO₃, respectively (13.58%).

The results of FT-IR spectra, XRD patterns, and DSC-TGA analysis can confirm the proposed structure (Scheme 1).

3.2. Catalytic applications of 1 in the epoxidation of alkenes

The epoxidation of *cis*-cyclooctene with **1** using tert-BuOOH as oxidant was studied as the model reaction under optimized conditions under reflux (Table 1). The effects of different solvents (Table 1, entries 3–7), mg of catalyst (Table 1, entry 7 and entries 12–15), oxidant type (Table 1, entries 7–10), mol % for catalyst loading (0.35–1.375 mol %), and oxidant to substrate molar ratio (0.2–2.24) for **1** were investigated. The results show that TBHP is the only oxidizing system, which can epoxidize cyclooctene in



Scheme 1. Reaction scheme for the synthesis of 1 nanohybrid.

Entry	Catalyst (mg)	Solvent ^b	Oxidant	Catalyst loading (mol%) ^c	Oxidant/Substrate molar ratio	Epoxide yield (%) ^d
1	Catalyst-free	C₂H₄Cl₂	ТВНР	_	2.24	_
2	H ₃ PMo ₁₂ O ₄₀	$C_2H_4Cl_2$	TBHP	-	2.24	trace
3	I(15)	CH₃OH	TBHP	1.375	2.24	18
4	I(15)	CCI ₄	TBHP	1.375	2.24	95
5	I(15)	CH_2CI_2	TBHP	1.375	2.24	78
6	I(15)	CHCI₃	TBHP	1.375	2.24	87
7	I(15)	$C_2H_4CI_2$	TBHP	1.375	2.24	99
8	I(15)	$C_2H_4CI_2$	H_2O_2	1.375	2.24	23
9	1 (15)	$C_2H_4CI_2$	$H_2O_2.CON_2H_4$	1.375	2.24	15
10	I(15)	$C_2H_4CI_2$	NalO ₄ ^e	1.375	2.24	trace
11	I(15)	CH₃CN	H_2O_2	1.375	2.24	57
12	I(10)	$C_2H_4CI_2$	TBHP	0.917	2.24	99
13	I(7)	$C_2H_4CI_2$	TBHP	0.642	2.24	99
14	I(5)	$C_2H_4CI_2$	TBHP	0.458	2.24	75
15	I(3)	$C_2H_4CI_2$	TBHP	0.275	2.24	42
16	I(7)	$C_2H_4CI_2$	TBHP	0.642	2.24	99
17	I(7)	$C_2H_4CI_2$	TBHP	0.642	1.68	75
18	I(7)	$C_2H_4CI_2$	TBHP	0.642	1.12	51
19	I(7)	CH₃OH	TBHP	0.35	0.2	30

Table 1. Epoxidation of cis-cyclooctene at refluxed conditions.^a

^aThe time of reactions is 30 min.

^bThe amount of solvent is 2 mL.

^cCalculated for 0.5 mmol cyclooctene.

^dGC yields are based on the starting cyclooctene.

^eTetra-butyl phosphonium bromide was used as phase transfer reagent.



Figure 7. Epoxidation of 0.5 mmol *cis*-cyclooctene with 1.12 mmol TBHP catalyzed by 7 mg of 1 in $2 \text{ mL } C_2H_4Cl_2$ under reflux.

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Fntrv	Alkene	Conversion (epoxide) (%) ^b	Selectivity (%)	Time (min)
1	Cyclooctene	99(99)	100	30
2	Cyclohexene	98(90) ^c	92	30
3	1-Octene	58(58)	100	90
4	1-Hexene	63(63)	100	90
5	Styrene	85(78) ^d	92	90
6	α-Methylstyrene	90(82) ^e	91	60
7	α-Pinene	87(80)	92	60
8	trans-Stillene	92(92) ^f	100(<i>trans</i>) ^g	60
9	<i>cis</i> -Stilbene	(90) ^f	78(<i>cis</i>) and 12 (<i>trans</i>) ^h	60

Table 2	. Epoxid	ation o	f some	olefins	with	TBHP	catalyz	ed	by	1 under	reflux.ª	
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^aReaction conditions: alkene (0.5 mmol), TBHP (1.12 mmol), catalyst (7 mg), C₂H₄Cl₂ (2 mL).

^bGC yield based on the starting alkenes.

^cThe by-product is 8% for the catalyst.

^dThe by-product is 7% for the catalyst.

^eThe by-product is 8% for the catalyst.

^fBoth ¹H NMR and GC data approved the reported yields.

⁹*Trans* isomer is the only product according to ¹H NMR data.

^hCis and trans isomers are both produced according to ¹H NMR data.

 $C_2H_4Cl_2$. Other oxygen sources like hydrogen peroxide, sodium periodate (in the presence of 0.01 g tetra-butyl phosphonium bromide as phase transfer reagent) and ureahydrogen peroxide in $C_2H_4Cl_2$ do not show activity (Table 1, entries 7–11). Figure 7 shows the effect of reaction time on the epoxidation of cyclooctene with TBHP. Reactivity of **1** achieves the maximum and becomes constant after 30 min.

Finally epoxidation of several olefins including linear, cyclic, and phenyl-substituted olefins with tert-butyl hydroperoxide as oxidant were performed in the presence of **1** (Table 2); electron-rich olefins are more reactive than electron-poor ones. Comparison

Entry no.	Catalyst	Substrate	Solvent	Time (h)	TOF (h^{-1})	Conv. (%)	Sel. (%)	Ref.
1	1	Cyclooctene	$C_2H_4Cl_2$	0.5	396	99	99	This work
2	PW4–C18	Cyclooctene	ĊH₃CN	5	6.83	96	99	[40]
3	BTE-PW ₁₁ O ₃₉	Cyclooctene	CH ₃ CN	1.5	-	99	>99	[41]
4	As ₈ V ₁₄ O ₄₂ (H ₂ O)] [Cu(2,2'-bpy) ₂] ₄	Cyclooctene	CH ₃ CN	9	-	65.5	100	[42]
5	[As ₈ V ₁₄ O ₄₂ (H ₂ O)] [Cu(1,10-phen) ₂] ₄	Cyclooctene	CH_3CN	9	_	33	100	[42]
6	PW ₁₂ /MIL-101	Cyclooctene	CH₃CN	3	0.38	76	99	[43]
7	MimAM(H)-PW	Cyclooctene	CH ₃ CN	4	-	95	100	[12]
8	${[Ag_2(trz)_2] [Ag_{24}(trz)_{18}]}$ [PMo ₁₂ O ₄₀]2	Cyclooctene	CH ₃ CN	3	-	96	-	[44]
9	[Cu ¹ ₆ (3atrz) ₆][PMo ₁₂ O ₄₀] ₂	Cyclooctene	1,4-dioxane	10	-	66	99	[45]
10	$[H_x PMo_{12}O_{40} \subset H_4 Mo_{72} \\ Fe_{30}O_{254} (CH_3 COO)_{15} (H_2 O)_{98}]$	Cyclooctene	ethanol	3.25	-	82	98	[46]

Table 3. The catalytic activity of various catalysts for the epoxidation of cyclooctene.

Table 4. Epoxidation of cis-cyclooctene with TBHP under reflux using recycled catalysts.^a

Number of cycles	Epoxide yield (%) ^b	TOF^{c} (h^{-1})	Amount of Mo leached (%) ^d
1	98	392	1
2	95	380	0.5
3	93	372	0
4	90	360	0
5	90	360	0
6	88	352	0

^aReaction conditions: 0.5 mmol cyclooctene, 1.12 mmol TBHP, 7 mg catalyst, 2 mL $C_2H_4Cl_2$, 30 min. ^bGC yields are based on the starting cyclooctene.

^cTOF = (Number of molecules reacted)/(Number of sites) \times (time).

^dDetermined by ICP.

of 1 with other reported catalysts in the epoxidation of cyclooctene is given in Table 3. Swalus et al. reported epoxidation of cyclooctene catalyzed by PW4-C18 compound [40]. The epoxidation reaction was performed using CH_3CN as a solvent giving epoxide products with a yield of 96% and excellent selectivities (Table 3, entry 2). Zhang et al. applied BTE-PW₁₁O₃₉ as a catalyst for olefin epoxidation using H₂O₂ as an oxidant in CH₃CN (Table 3, entry 3) [41]. Conversion and selectivity toward the epoxide were 99%. Guo et al. found that two complexes $[As_8V_{14}O_{42}(H_2O)][Cu(2,2'-bpy)_2]_4$ and [As₈V₁₄O₄₂(H₂O)][Cu(1,10-phen)₂]₄, which were synthesized by the hydrothermal method, were applied to the selective epoxidation of olefins [42]. In acetonitrile as solvent, 64.5% conversion and 100% selectivity for compound 1 and for compound 2, 33% conversion and 100% selectivity were reported (Table 3, entries 4 and 5). Maksimchuk et al. reported that PW12/MIL-101 used as a true heterogeneous catalyst can be recycled four times without loss of activity (Table 3, entry 6) [43]. Leng et al. demonstrated that the epoxidation of cyclooctene can be made with MimAM (H)-PW [12]. This group of researchers performed the oxidation reaction in acetonitrile as a solvent, and 95% conversion and 100% selectivity of epoxide were reported (Table 3, entry 7). Du et al. in 2019 reported that the oxidation reaction performed in acetonitrile with $\{[Ag_2(trz)_2][Ag_{24}(trz)_{18}]\}[PW_{12}O_{40}]_2$, giving 3 h 96% conversion [44]. Jia et al. reported the catalytic activity of [Cu¹₆(3atrz)₆][PMo₁₂O₄₀]₂ in the epoxidation of various alkenes (Table 3, entry 9) [45]. Taghiyar and Yadollahi carried out the epoxidation of cyclooctene catalyzed by $[H_x PMo_{12}O_{40} \subset H_4 Mo_{72}Fe_{30}O_{254}(CH_3COO)_{15}(H_2O)_{98}]$ in



Figure 8. Reusability of **1** for the oxidation of *cis*-cyclooctene at optimum conditions. Reaction conditions: 0.5 mmol cyclooctene, 1.12 mmol TBHP, 7 mg catalyst, 2 mL C₂H₄Cl₂, 30 min.



Figure 9. FT-IR spectra of recovered 1 nanocatalyst.

ethanol with conversion and selectivity toward epoxide of 82% and 98% [46]. In the present work, **1** gives 100% conversion and 100% selectivity for epoxidation of cyclooctene in 30 min (Table 3, entry 1). Therefore, the present catalysts display the desired catalytic activity for epoxidation of alkenes compared to other catalysts listed in Table 3.

The reusability of **1** was studied for oxidation of *cis*-cyclooctene as a model reaction using tert-butyl hydroperoxide at optimum conditions. In each experiment, after completion of the reaction, the catalyst was separated from the reaction mixture by centrifugation, washed several times with 1,2-dichloroethane, dried, and then, reused in the same reaction. The results are given in Table 4. As shown in Figure 8 the recovered catalysts were reused at least six times without losing activity. These results prove that the catalytic reactions are retained and the catalysts are not leached to the reaction medium. The decrease in cyclooctene conversion could be attributed mainly to

unavoidable loss of the catalyst during collection. The average values of cyclooctene conversion and epoxide selectivity were 93% and 99%, respectively. The results confirm that **1** has good stability for the oxidation of cyclooctene under our investigation conditions. Furthermore, ICP has been employed to detect/determine the amount of metal that leached out into the reaction mixture. No detectable molybdenum was found in the reaction mixtures. The IR spectra of recovered catalysts did not show any obvious differences from fresh catalysts (Figure 9).

4. Conclusion

We have prepared a nanohybrid heterogeneous catalyst by combination of molybdenylacetylacetonate and Schiff base with polyoxometalates and tested its catalytic activity in the synthesis of various epoxides carried out via reaction olefins with **1** nanocatalyst and using tert-butyl hydroperoxide as oxidant. This catalytic system combines the benefits of biphasic and heterogeneous catalysis, allowing easy separation of products and catalysts. This catalyst is recyclable, reused at least six times without significant loss in its catalytic activity.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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