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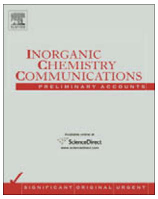

Polyoxometalate–molybdenylacetylacetonate hybrid complex: A reusable and efficient catalyst for oxidation of alkenes with *tert*-butylhydroperoxide

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The hybrid complex consist of molybdenylacetylacetonate complex covalently linked to a lacunary Keggin-type polyoxometalate, $K_8[SiW_{11}O_{39}]$ (POM), was synthesized and characterized by elemental analysis, SEM, XRD, diffuse reflectance UV–Vis and FT-IR spectroscopic methods. The hybrid complex, $[MoO_2(acac)–POM]$ (**1**), was used for alkene epoxidation with *tert*-BuOOH in 1,2-dichloroethane as solvent. The complex (**1**) can catalyze epoxidation of various olefins including non-activated terminal olefins. The effect of reaction parameters such as oxidant, solvent, and temperature on the epoxidation of cyclooctene was also investigated. This heterogeneous catalyst was reused several times in the oxidation of cyclooctene.

Applying and using heterogeneous catalysts offers numerous advantages in contrast to corresponding homogeneous compounds. For instance, better stability, separation, and simple recovery and recycling. Distinct methodologies have been developed for the immobilization of homogeneous catalysts or the creation of heterogeneous catalysts [1]. Heterogeneous catalysts have played a vast role in many reactions such as oxidation. Academic and industrial interest is drawn to epoxidation of alkenes and reaction products based on epoxides [2]. Surfactants, detergents, antistatic agents and corrosion protection agents, lubricating oils, textiles and cosmetics are technically vital products obtained from the reaction of epoxides [3]. Above all, valuable organic intermediates such as cyclooctene and cyclohexene oxides are employed in the synthesis of pesticides, chiral pharmaceuticals, rubber promoters, epoxy paints and dyestuff products [4].

Among the various metals used as catalysts, molybdenum is one of the most important. It is the only second row transition metal essential for life. Many homogeneous and heterogeneous catalysts of molybdenum have been synthesized and used up to date [5–11], especially in the oxidation of alkenes [12–16], sulfoxidation and hydrosilylation of carbonyl groups [17], hydrodesulfurization [18], synthesis of metal containing polymers [19], optical and electrochemical sensors to enhance selectivity and sensitivity [20], DNA interactions [21], nitrate reduction [22–24], and lots of other reactions. Several heterogeneous dioxomolybdenum(VI) complexes have also been synthesized [25–27] and have been good catalyst precursors for olefin epoxidation [28,29].

Many catalysts show good results when hybridized. Among some capable hybrid compounds are metal–organic–polyoxometalates [30] and metal Schiff bases hybridized with polyoxometalates [31]. Several of these metal complexes have been synthesized and studied towards various reactions [32–36]. A major drawback in these catalysts is that they are homogeneous and have difficulties in being separated. Different approaches have been used to turn homogenous catalysts into heterogeneous counterparts by hybridizing different materials.

In this article, a hybrid compound, by combining the properties of molybdenylacetylacetonate and a Keggin-type polyoxometalate, was synthesized and used as a heterogeneous and efficient catalyst for the epoxidation of olefins with *tert*-BuOOH. The effect of different solvents, oxidants, and temperatures on the activity and selectivity of the catalyst was also studied (Scheme 1).

The $MoO_2(acac)_2$ was prepared as reported in the literature [37]. The lacunary Keggin-type polyoxometalate, $K_8[SiW_{11}O_{39}]$ (POM) was prepared and characterized as reported by Tézé and Hervé [38], and the tetrahexylammmonium salt of $\{SiW_{11}O_{39}[O(SiR)_2]\}^{4-}$ in which R is $CH_2CH_2NH_2{\cdot}HCl$ was synthesized as reported by Neumann and coworkers [31].

The $[MoO_2(acac)–POM]$ complex was synthesized using the $Q_4\{SiW_{11}O_{39}[O(SiR)_2]\}$ precursor and a modified procedure (Scheme 2) [39]. Several attempts to prepare its single crystal were failed. Therefore, hybrid complex was characterized by elemental analysis, SEM, diffuse reflectance UV–Vis and FT-IR spectroscopic methods and powder X-ray diffraction.

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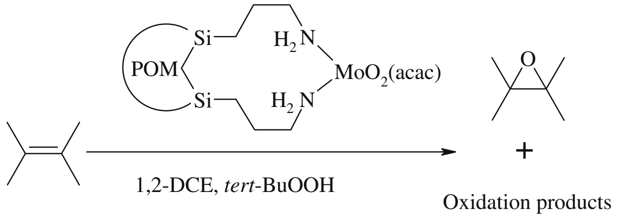


Scheme 1.

Primary evidence of the electronic effect of the polyoxometalate on the $MoO_2(acac)_2$ was observed in the UV–Vis spectra. As seen in Fig. 1, the hybrid MoO_2(acac)–POM, has a different UV–Vis spectrum from the un-hybrided $MoO_2(acac)_2$. The $MoO_2(acac)_2$ has a λ_{max} at 410 nm which is recognized as the $O(p_\pi) \rightarrow Mo(d_\pi)$ charge-transfer transition [40]. This is shifted to 362 nm in the MoO_2(acac)–POM complex. This shift may be deducted to an intramolecular effect of the POM on the $MoO_2(acac)_2$ and/or strong sigma donor nature of the amine ligands, when one of the acac ligands is replaced with two strong sigma donors ligands such as amine, it is expected that the energy of the LMCT band increases.

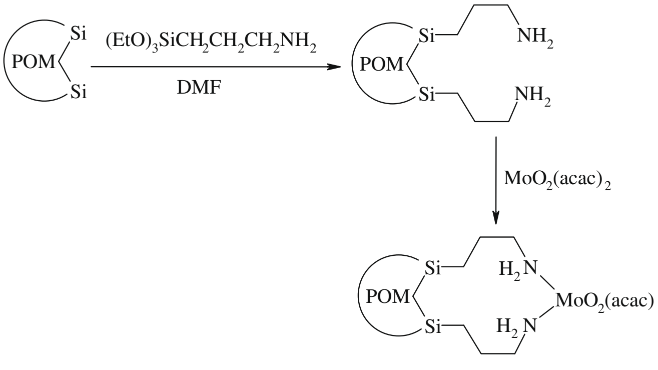
The SEM images show different morphological surfaces for pure POM and the referring MoO_2(acac)–POM (Fig. 2). The amount of Mo loading in the supported catalyst was determined by ICP, which showed a value of 0.198 mmol per gram of catalyst. The FT-IR spectra shows two distinct bands at 918 and 973 cm^{-1} which are attributed to Mo=O vibrations (Fig. 3).

The XRD pattern of POM and [MoO_2(acac)–POM] are shown in Fig. 4. As can be seen, it is clear that $MoO_2(acac)_2$ has been successfully supported on POM.

The catalytic activity of the prepared catalyst was tested using cyclooctene as reference alkene. Oxidation was carried out with *tert*-BuOOH as an oxidant and in the presence of catalytic amounts of [MoO_2(acac)–POM]. The optimum conditions used for the oxidation of cyclooctene by this catalytic system was catalyst, oxidant, and substrate in a molar ratio of 1:150:63, respectively. To further optimize the conditions, different solvents were also used in the oxidation of cyclooctene with *tert*-BuOOH. The results showed that the highest yield obtained in 1,2-dichloroethane and even though dichloromethane and chloroform also had high yields (Table 1).

The effect of different oxidants such as H_2O_2, $NaIO_4$, *tert*-BuOOH and H_2O_2/Urea (UHP) was also investigated in the oxidation of cyclooctene. The results showed that *tert*-BuOOH is the best oxygen source (Table 2).

The reaction temperature was also optimized by repeating the reaction in various temperatures. At room temperature (25 °C), the product yields were low and with increasing the reaction temperature to 75 °C (refluxing 1,2-DCE), both the conversion and selectivity increased (Table 3).



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Scheme 2.

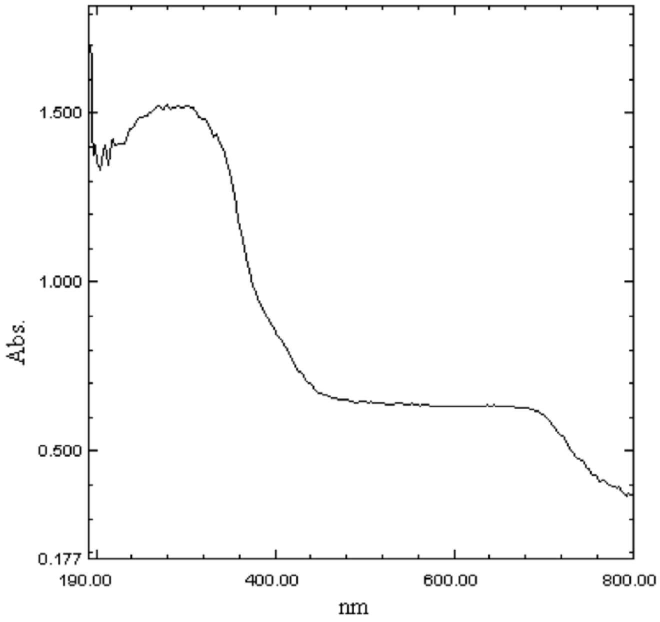


Fig. 1. DR UV–Vis spectrum of [MoO_2(acac)–POM].

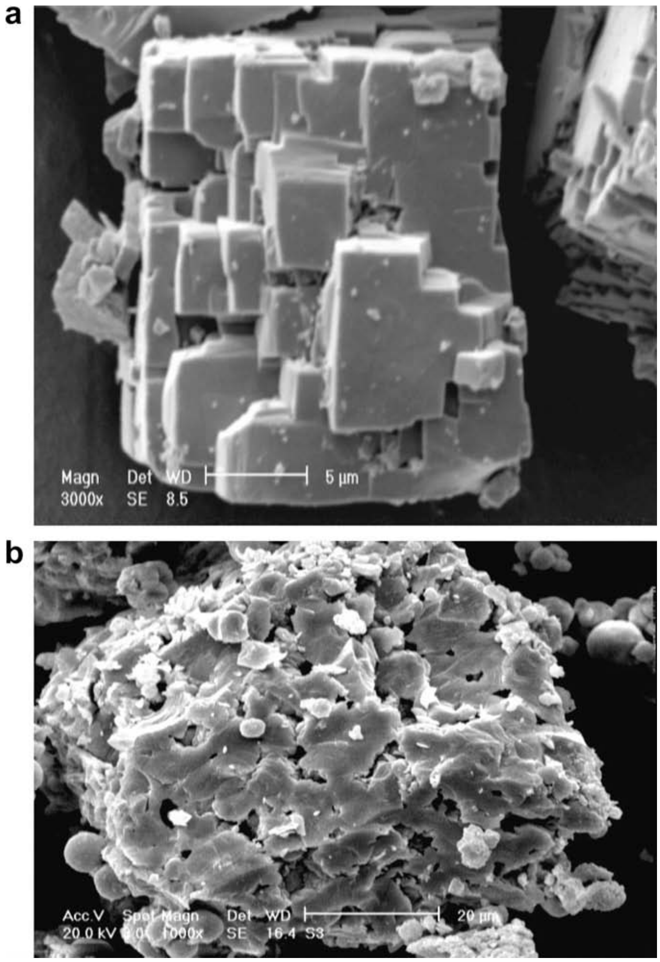


Fig. 2. SEM image of: (a) Keggin-type polyoxometalate, $K_8[SiW_{11}O_{39}]$ (POM), and (b) [MoO_2(acac)–POM].

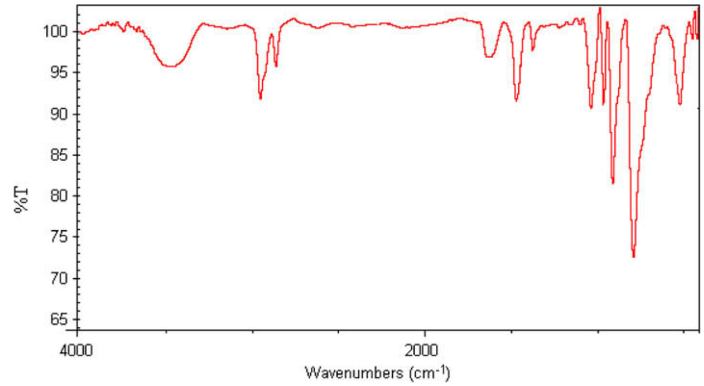


Fig. 3. FT-IR spectrum of [MoO_2(acac)–POM].

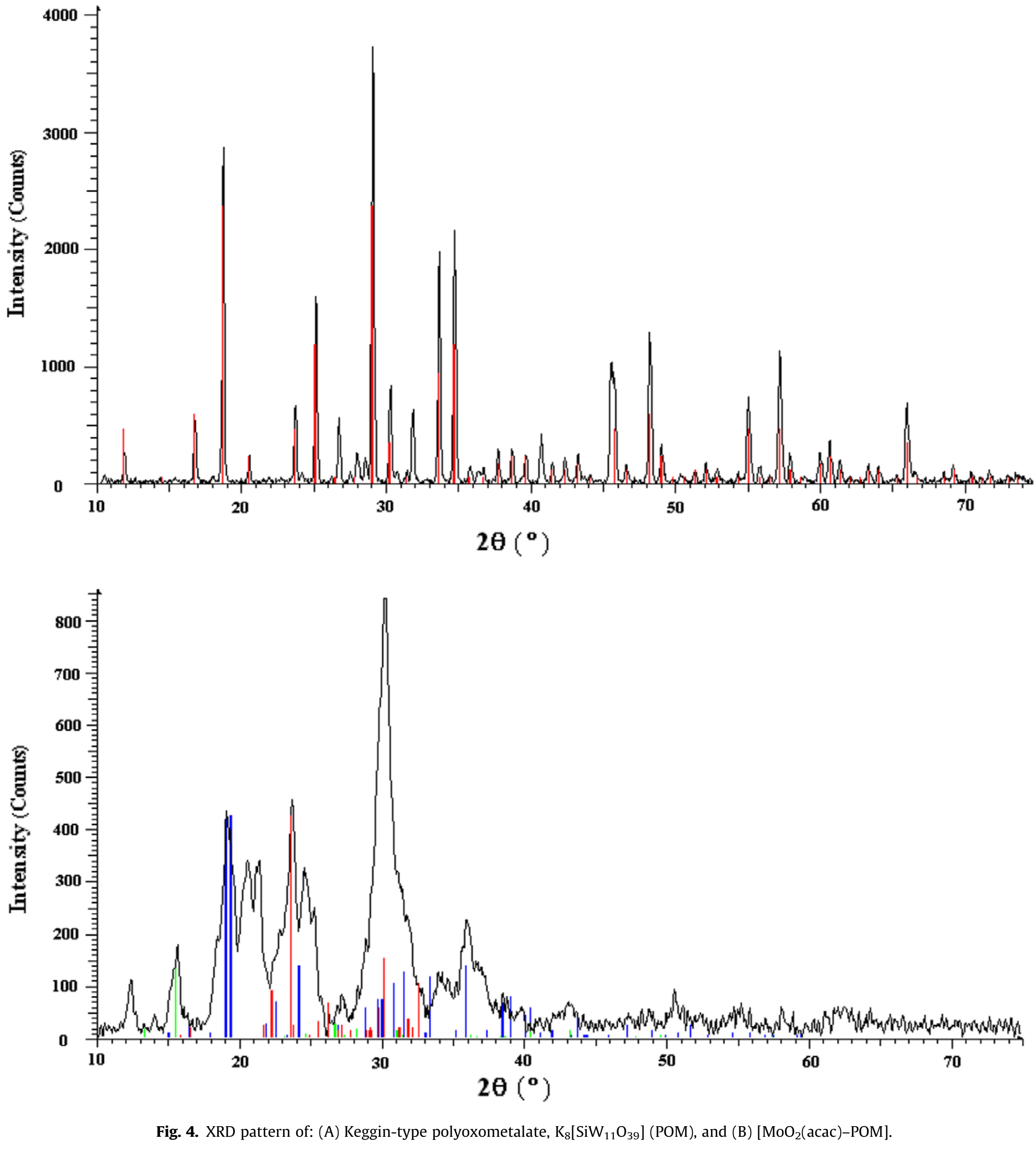


Fig. 4. XRD pattern of: (A) Keggin-type polyoxometalate, $K_8[SiW_{11}O_{39}]$ (POM), and (B) [MoO_2(acac)–POM].

Table 1
Effect of solvent on the oxidation of cyclooctene catalyzed by [MoO_2(acac)–POM] under reflux conditions.[a]

Row	Solvent	Conversion (%)[b] after 8 h
1	1,2-Dichloroethane	100
2	CH_2Cl_2	90
3	CH_3COCH_3	44
4	CCl_4	59
5	CH_3CN	50
6	$CHCl_3$	95

[a] Reaction conditions: cyclooctene (0.5 mmol), *tert*-BuOOH (1.5 mmol), catalyst (0.008 mmol), solvent (2 ml).
[b] GC yield.

Table 2
Effect of different oxidants on the oxidation of cyclooctene catalyzed by [MoO_2(acac)$_2$–POM] under reflux conditions.[a]

Row	Oxidant	Solvent	Conversion (%)[b] after 8 h
1	H_2O_2	1,2-DCE	8
2	$NaIO_4$	H_2O/CH_3CN	36
3	H_2O_2/Urea (UHP)	1,2-DCE	30
4	*tert*-BuOOH	1,2-DCE	100
5	No oxidant	1,2-DCE	trace

[a] Reaction conditions: cyclooctene (0.5 mmol), oxidant (1.5 mmol), catalyst (0.008 mmol).
[b] GC yield.

Table 3
Effect of temperatures on the oxidation of cyclooctene catalyzed by [MoO_2(acac)–POM].[a]

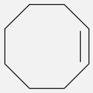
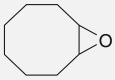
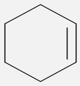
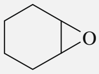
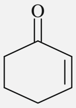
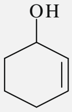
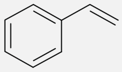
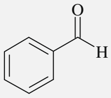
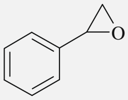
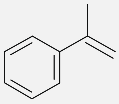
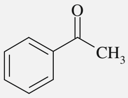
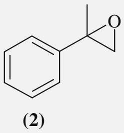
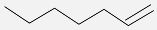
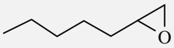
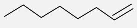
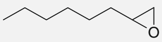
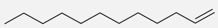
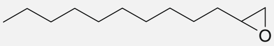
Row	Temperature (°C)	Conversion (%)[b] after 8 h
1	25	6
2	40	40
3	60	43
4	75 (reflux)	100

[a] Reaction conditions: cyclooctene (0.5 mmol), *tert*-BuOOH (1.5 mmol), catalyst (0.008 mmol), 1,2- DCE (2 ml).
[b] GC yield.

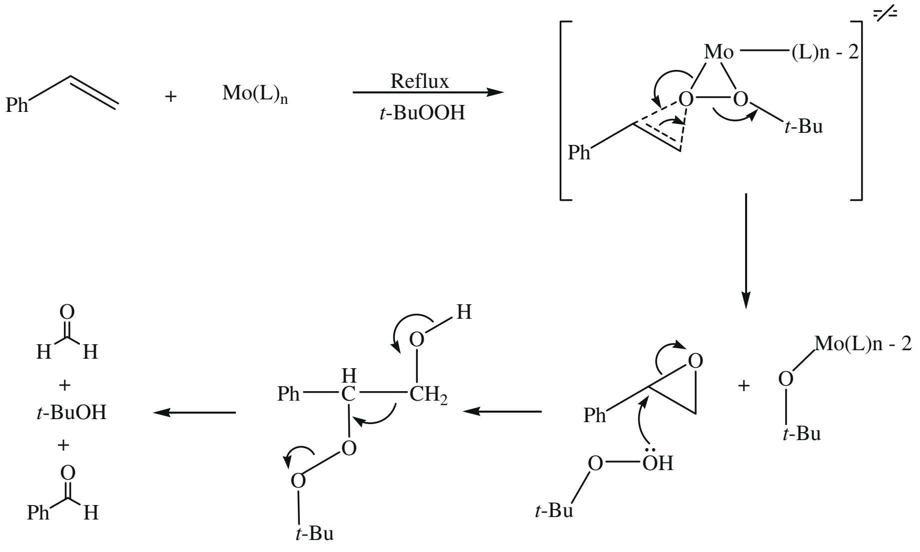
Under the optimized conditions which obtained for oxidation of cyclooctene, different alkenes such as cyclohexene, styrene, α-methylstyrene, 1-heptene, 1-octene and 1-dodecene were oxidized. The results are shown in Table 4 [41]. Clearly, electron rich olefins are more reactive than electron poor ones. In the case of cyclooctene, the cyclooctene oxide was the selective product with 100% yield. Oxidation of cyclohexene gave an allylic oxidation product, 2-cyclohexene-1-one, which was also the major product, with 92% yield. In this case the alcohol and enone can arise via allylic oxidation or via Lewis acid catalyzed rearrangement of the epoxide, and subsequent elimination and secondary oxidation. To check this, a base such as pyridine was added to the reaction mixture. The results showed that the distribution of products were as observed in the absence of pyridine. These observations indicated that the products were aroused via allylic oxidation. With styrene and α-methylstyrene the major products were benzaldehyde and acetophenone, respectively. These products are resulted from the attack of *t*-BuOOH to epoxide and cleavage of the respected intermediated as shown in the proposed mechanism (Scheme 3). These results show that the conjugation of aromatic ring with carbonyl group stabilizes the products. The great feature of the catalytic epoxidation with MoO_2(acac)–POM is that non-activated terminal olefins such as 1-heptene and 1-octene, could be proficiently transformed to the corresponding epoxides in high yields.

It was found that the alkenes were not oxidized in the absence of catalyst or oxidant. Mizuno and coworkers have already examined the epoxidation of olefins with H_2O_2 catalyzed by mono- and tri-vacant lacunary compounds such as [α-$SiW_{11}O_{39}$]$^{8-}$ and

Table 4
Oxidation of alkenes with TBHP catalyzed by [MoO_2(acac)–POM].[a]

Entry	Alkene	Product[a]	Conversion (%)[b]	Selectivity (%)[b]	Time (h)	TOF (h^{-1})
1			100	100	8	7.81
2		 **(1)**  **(2)**  **(3)**	96	(1) 4 (2) 95 (3) 1	6	10.00
3		 **(1)**  **(2)**	94	((171 ((2 29	8	7.35
4		 **(1)**  **(2)**	98	(1) 95 ((25	8	7.66
5			100	100	8	7.81
6			91	91	8	7.11
7			17	17	8	1.38

[a] Reaction conditions: alkene (0.5 mmol), *tert*-BuOOH (1.5 mmol), catalyst (0.008 mmol), 1,2-dichloroethane (2 ml), *T* = 75 °C.
[b] GLC yield based on starting alkene.



Scheme 3.

Table 5
Investigation of [MoO_2(acac)–POM] reusability in the epoxidation of cyclooctene.[a]

Run	Conversion (%)[b] after 8 h	Amount of Mo leached (%)[c]
1	100	2.5
2	88	0
3	88	0
4	88	0

[a] Reaction conditions: cyclooctene (0.5 mmol), *tert*-BuOOH (1.5 mmol), catalyst (0.008 mmol), 1,2-DCE (2 ml), $T = 75$ °C.
[b] GC yield.
[c] Determined by ICP.

[α-SiW_9O_{34}]$^{10-}$ and showed that these compounds were inactive [42]. Here, we used *tert*-BuOOH towards oxidation of cyclooctene in the presence of only polyoxometalate and the results were the same, indicating that the polyoxometalate was almost inactive.

The most advantage of MoO_2(acac)–POM catalyst is its heterogeneous nature in the oxidation reactions. Therefore, this heterogeneous catalyst can be easily recovered and reused.

In order to show the reusability of the catalyst, cyclooctene was used as model substrate. The reactions were performed as described above. At the end of the reaction, the catalyst was filtered and reused in the next run. The results showed that after the first run, the amount of epoxides was 88%. This is due to the leaching phenomenon, in which about 2.5% of initial Mo is leached in the first run. In the next runs, no Mo was detected in the reaction mixture (Table 5). To check that whether released Mo is being absorbed on the POM surface or bonded to POM, the catalyst has been washed thoroughly with water, methanol and diethyl ether, and used for epoxidation of cyclooctene with *tert*-BuOOH. The results showed that the same amount of leaching was observed. This may due to the trapped Mo which is not been washed with solvent.

In conclusion, we observed that the catalytic activity of MoO_2(acac)$_2$ can be modified by a Keggin-type polyoxometalate through covalent bonding. A strong electronic effect was observed upon attachment of polyoxometalate, leading to an intramolecular charge separation and description of (**1**) as a charge-transfer complex [31,43,44]. The complex (**1**) exhibits a good catalytic activity in the oxidation of various olefins including non-reactive terminal olefins. The MoO_2(acac)–POM catalyst is a heterogeneous catalyst and can be easily separated and reused.

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[39] *Experimental.* All materials were of commercial reagent grade and prepared from Merck, Aldrich or Fluka. Alkenes were obtained from Merck or Fluka and were passed through a column containing active alumina to remove peroxide impurities. Scanning electron microscopy (SEM) images were taken using a Phillips XL 30 model. FT Infrared (FT-IR) spectra were obtained as potassium bromide pellets in the range of 400–4000 cm^{-1} with a Nicolet Impact 400D instrument. Gas chromatography experiments (GC) were performed on a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 m. Diffuse reflectance UV–Vis (DR UV–Vis) spectra were obtained on a Shimadzu UV 265 spectrometer using $BaSO_4$ as reference compound. $Q_4\{SiW_{11}O_{39}[O(SiR)_2]\}$ (1.5 g, 0.32 mmol) was dissolved in degassed DMF (5 ml), and heated to 75 °C. A solution of $MoO_2(acac)_2$ (0.106 g, 0.32 mmol) was added and the reactants were maintained for an additional 2 h before being cooled. Methanol (30 ml) was added to attain the precipitate (pale yellow color), which was carefully washed with methanol and ether before vacuum drying.
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[41] *General procedure for oxidation reactions.* All reactions were carried out in a 25 ml glass reactor which was equipped with a reflux condenser and a gas inlet. In a typical procedure, a mixture of catalyst (**1**) (40 mg, 0.008 mmol), alkene (0.5 mmol), *tert*-BuOOH (1.5 mmol) in 1,2- dichloroethane (2 ml) was prepared. The reaction progress was monitored by GC. At the end of the reaction, the catalyst was filtered. Then, the solvent was evaporated and the crude product was purified on a silica-gel column. The identities of the products were confirmed by ^1H NMR and IR spectral data.
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