A one-dimensional polyoxomolybdate polymer as catalyst for the epoxidation of olefins

Epoxidation reaction was carried out by refluxing the mixture of substrate and oxidant in a given solvent in the presence of the catalyst. After the reaction, the catalyst was separated and the filtrate was analyzed by NMR, GC and GC-Mass.

NMR analyses:

¹H and ¹³C NMR analyses for the epoxidation of cyclooctene as the representative substrate are shown in Fig. S1. The NMR spectra confirm the formation of epoxycyclooctane product.







b)

Fig. S1. (a) ¹H and (b) ¹³C NMR for the epoxidation of cyclooctene in the presence of $\{(NH_4)_4Mo_8O_{26}\}_n$ (1). Reaction conditions: cyclooctene (8 mmol), TBHP (14.4 mmol), CHCl₃ (10 ml), catalyst (50 mg), time (120 min).

GC analysis:

The GC data and chromatograms for the epoxidation of cyclooctene are provided in Fig. S2. In the chromatograms, the peak observed in the retention time of 1.081 min is related to the CHCl₃ as solvent. The peaks appeared in the retention times of about 1.7 and 2.8 min are relevant to the oxidant. The peaks observed in the retention time of about 5.7 and 10 min are due to cyclooctene substrate and epoxycyclooctane product, respectively. As the reaction proceeds from 15 to 120 min (Fig. S2a-S2e), the peak area for the substrate decreases while the peak area for the epoxide product increases.





Fig. S2. GC analyses for the epoxidation of cyclooctene in the presence of $\{(NH_4)_4Mo_8O_{26}\}_n$ (1). Reaction conditions: cyclooctene (8 mmol), TBHP (14.4 mmol), CHCl₃ (10 ml), catalyst (50 mg), time (a) 15, (b) 30, (c) 45, (d) 60 and (e) 120 min.

The chromatogram and the mass data for the epoxidation of cyclohexene are presented in Fig. S3. In the chromatogram, the peak in the retention time of about 1.1 min is due to $CHCl_3$ as solvent. The peaks observed in the retention times of about 1.8 and 2.9 min are relevant to the oxidant. The peak appeared in the retention time of about 4.9 is related to epoxycyclohexane product that is confirmed by the mass spectrum.



Fig. S3. GC chromatogram and the corresponding mass spectra for the epoxidation of cyclohexene in the presence of $\{(NH_4)_4Mo_8O_{26}\}_n$ (1). Reaction conditions: cycloohexene (8 mmol), TBHP (14.4 mmol), CHCl₃ (10 ml), catalyst (50 mg), time 120 min.

Fig. S4 shows the GC chromatogram and the mass data for the epoxidation of styrene. The peak observed in the retention time of about 9.4 min is due to the epoxystyrene that is confirmed by mass spectrum.



Fig. S4. GC chromatogram and the mass spectra for the epoxidation of styrene in the presence of $\{(NH_4)_4Mo_8O_{26}\}_n$ (1). Reaction conditions: styrene (8 mmol), TBHP (14.4 mmol), CHCl₃ (10 ml), catalyst (50 mg), time 8 h.

The chromatogram for the epoxidation of 1-hexene is shown in Fig. S5A. In the chromatogram, the peak in the retention time of about 4.2 min is related to epoxyhexane product and the peak for the 1-hexene substrate is not observed (Fig. S5A). After the addition of standard 1-hexene to this mixture, a new peak is appeared in the retention time of 1.755 min (Fig. S5B). This peak is not observed in Fig. S5A indicating that the 1-hexene substrate is converted to the corresponding epoxide after 24 h of the reaction.



Fig. S5. (A) GC chromatogram for the epoxidation of 1-hexene in the presence of $\{(NH_4)_4Mo_8O_{26}\}_n$ (1) (Reaction conditions: 1-hexene (8 mmol), TBHP (14.4 mmol), CHCl₃ (10 ml), catalyst (50 mg), time 24 h) and (B) the chromatogram of the mixture of A solution and standard 1-hexene substrate.

The injection of standard 1-octene (Fig. S6A) and epoxyoctane (Fig. S6B) shows that 1-octene appears in the retention time of 4.59 and epoxyoctane is observed in the time of 8.37 min. The chromatogram for the epoxidation of 1-octene is shown in Fig. S6C. In the chromatogram, the peak in the retention time of about 8.4 min is due to epoxyoctane product.



Fig. S6. (A) GC chromatogram of the standard solution containing chloroform and 1-octene, (B) the chromatogram of standard epoxyoctane and (C) the chromatogram for the epoxidation of 1-octene in the presence of $\{(NH_4)_4Mo_8O_{26}\}_n$ (1) (Reaction conditions: 1-octene (8 mmol), TBHP (14.4 mmol), CHCl₃ (10 ml), catalyst (50 mg), time 22 h).