Epoxidation of allylic alcohols on self-assembled polyoxometalates hosted in layered double hydroxides with aqueous H_2O_2 as oxidant

Peng Liu, Changhao Wang, Can Li *

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

ABSTRACT

A series of self-assembled polyoxometalate (POM) catalysts were directly immobilized into layered double hydroxides (LDH) by a selective ion-exchange method. Sandwich-type POM species are found to be more favorable than Keggin-type POM for the direct immobilization in LDH, because strict pH controlling is not needed and the LDH hosts can be kept intact. The resulting LDH–POM catalysts were evaluated in the epoxidation of allylic alcohols with aqueous H_2O_2 as the oxidant without using organic solvent. The heterogeneous LDH–POM catalysts show much higher epoxide selectivity than the corresponding homogeneous Na–POM catalysts, which can be attributed to the beneficial effect of basic LDH host on the suppression of the acid-catalyzed epoxide hydrolysis. The cooperation between the POM guest and the LDH host can achieve up to 99% selectivity of epoxide, 95% H_2O_2 efficiency and 37200 h^{-1} TOF without the need of base additives and pH controlling, and the host-guest catalysts can be readily recycled with no apparent loss of catalytic performance.

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1. Introduction

The development of efficient and practical epoxidation technologies that utilize aqueous H_2O_2 as the oxidant is a subject of considerable academic and industrial interest [1,2]. Among various homogeneous epoxidation catalysts, polyoxometalates (POM) are more promising due to their oxidative stability and high efficiency [1–6]. However, there is still a challenge that the inherent acidity of POM catalysts and aqueous H_2O_2 may cause the hydrolysis of epoxide. Many approaches such as addition of basic pH-adjusting additives [7–11], insufficient amount of aqueous H_2O_2 [11–15], using phase transfer catalysts [7,11–27] and organic solvents [7–29] have been used to overcome this problem; however, these catalytic systems have a negative impact on the environment and cost efficiency, and often have difficulty in catalyst recovery. Given these limitations, there is substantial challenge for the development of heterogeneous POM catalysts that can suppress the acid-catalyzed hydrolysis of epoxide without the need for any added additives.

Hydrotalcite-like layered double hydroxides (LDH), so-called anionic clays, are known to possess surface basicity and interlayer anion-exchange capability [30–32]. It has been demonstrated that LDH meets the requirement of inorganic support for immobilizing anionic POM catalysts [31] and may provide a possibility for

protecting the epoxide against hydrolysis [33]. Various POM anions can be incorporated into LDH by a typical ion-exchange process to form LDH-hosted POM (LDH–POM) catalysts. Although a few of LDH–POM catalysts have been used for the H_2O_2-based epoxidation of olefins [34–42], most of them focus on the use of acid-stable POM species and request rigorous anhydrous H_2O_2 as the oxidant [34–39], which need toxic organic solvents. Furthermore, the limitation of low turnover frequency (TOF $<$ 10 h^{-1}) slows down the practical application of the LDH–POM catalysts.

Recently, we reported in a communication [43] on the direct immobilization of a self-assembled POM in LDH for heterogeneous epoxidation with aqueous H_2O_2. The self-assembled POM without isolation and purification can be selectively exchanged into LDH. To demonstrate the versatility and applicability of this new immobilization method and the as-prepared LDH–POM catalysts for solventless epoxidation, here we report on an extension of this work. A series of LDH–POM catalysts built up by different self-assembled POM complexes and LDH supports are compared. They were tested for the epoxidation of allylic alcohols with aqueous H_2O_2 in the absence of organic solvent, focusing on the selectivity distinction between heterogeneous and homogeneous catalysis. Our results suggest that the intact LDH host with surface basicity can suppress the acidity of epoxidation system. The cooperation of the POM guest and the LDH host can make a significant enhancement in the selectivity for the epoxidation of various allylic alcohols under mild and organic solvent-free conditions.

* Corresponding author. Fax: +86 411 84694447.
E-mail address: canli@dicp.ac.cn (C. Li).

2. Experimental

2.1. General

Na$_2$WO$_4$·2H$_2$O (>99%) and aqueous H$_2$O$_2$ (30 wt%; AR) were purchased from the Shenyang Chemical Reagent Factory. Phosphotungstic acid (H$_3$PW$_{12}$O$_{40}$·xH$_2$O; AR), Zn(NO$_3$)$_2$·6H$_2$O (>99%), Mg(NO$_3$)$_2$·6H$_2$O (>99%), and NaOH (>99%) were purchased from the Shanghai Chemical Reagent Company of the Chinese Medicine Group. 2-Buten-1-ol (97%) was supplied by Alfa Aesar. Prenol (98%) was obtained from TCI. *cis*-2-Penten-1-ol (98%), *cis*-2-hexen-1-ol (95%), *trans*-2-hexen-1-ol (96%), 3-methyl-3-buten-1-ol (97%), and geraniol (99%) were purchased from Acros Organics. All these reagents were used as received. Aqueous H$_2$O$_2$ was stored at 4 °C. Other reagents and solvents were obtained from commercial sources and used without purification unless otherwise stated.

X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT D/Max 2500 powder diffraction system (Cu$K\alpha$, 40 kV, 100 mA). FT-IR spectra were collected on a Thermo-Nicolet Nexus 470 infrared spectrometer, using the KBr pallet method at a resolution of 4 cm^{-1}. SEM micrograph and EDS analysis were taken using a FEI Quanta 200F scanning electron microscope equipped with an energy-dispersive X-ray spectrometer at an acceleration voltage of 20–30 kV. TEM micrographs were taken using a FEI Tecnai G^2 Spirit transmission electron microscope at an acceleration voltage of 120 kV. High-resolution transmission electron microscopy (HRTEM) study was conducted using a FEI Tecnai G^2 F30 S-Twin electron microscope equipped with a field emission gun, working at an acceleration voltage of 300 kV. ICP analysis was performed on a Leeman Plasma-Spec-II atomic emission spectrometer. The nitrogen sorption experiments were performed at 77 K on an ASAP 2000 system. The samples were outgassed at 120 °C for 6 h before the measurement. UV-Raman spectra were recorded on a homemade UV-Raman spectrometer. The laser line at 325 nm of a He–Cd laser was used as an exciting source with an output of 25 mW. The laser power on the sample is less than 3.0 mW.

The pH measurements were performed by using Cyberscan 510 pH meter. A qualitative measurement of the acid–base strength of solid samples was determined by Hammett indicators; 0.05 g sample was shaken with 2 mL indicator solution (0.01 g indicator in a mixture solution of 80 mL distilled water and 20 mL ethanol) and left to equilibrate for 2 h after which no further color changes were observed. The color on the sample was noted. The following Hammett indicators were used: phenolphthalein (pK_a 9.3), thymol blue (pK_2 8.8), cresol red (pK_2 8.1), bromothymol blue (pK_a 7.2), bromcresol purple (pK_a 6.0) and methyl red (pK_a 5.2). The concentration of surface base sites was evaluated by titration with 0.01 M benzoic acid solution in distilled water using 0.05 g of solid sample suspended in 2 mL of indicator solution. The indicator solution for the determination of basic sites contained 0.01 g of bromothymol blue (pK_a 7.2) in a mixture solution of 80 mL distilled water and 20 mL ethanol.

The reference epoxides were prepared by using homogeneous VO(acac)$_2$ catalyst (1–5 mol%) with t-BuOOH in isooctane. The purity of these compounds was confirmed by GC-MS (Agilent 6890N GC/5973 MS detector), and ^{1}H NMR (Bruker DRX-400). An internal standard method was used with n-dodecane as the internal standard in all epoxidation tests, hydrolysis tests and calibration runs. In the calibration runs, all allylic alcohols and corresponding reference epoxides were used to set up the calibration curves. Conversions and selectivities of all epoxidation reactions were analyzed by GC-FID using an Agilent 6890N GC with HP-19091G-B213 capillary column. The amount of H$_2$O$_2$ in the reaction mixture was determined by cerimetry [8]. 0.2 mL of the reaction mixture was diluted in 3 mL of distilled water and acidified with 0.5 mL of 1.0 M H$_2$SO$_4$. The resulting mixture was then titrated with a 0.1 M Ce(SO$_4$)$_2$ solution.

2.2. Preparation of catalyst precursors

2.2.1. Self-assembled [WZn$_3$(ZnW$_9$O$_{34}$)$_2$]$^{12-}$ (ZnWO) and [WCo$_3$(CoW$_9$O$_{34}$)$_2$]$^{12-}$ (CoWO)

The self-assembled ZnWO solution was prepared by gradual addition of aqueous Zn(NO$_3$)$_2$ to an aqueous solution of Na$_2$WO$_4$ and nitric acid, with the molar ratio of Zn(NO$_3$)$_2$/Na$_2$WO$_4$/HNO$_3$ = 5/19/16 [25,43]. In a typical procedure, Na$_2$WO$_4$·2H$_2$O (63.5 g, 190 mmol) was dissolved in water (200 mL) at 85 °C. At this temperature, aqueous 65% HNO$_3$ (12 mL, 175 mmol) was added. The yellow precipitate that was formed dissolved almost immediately, and the reaction mixture was heated to 95 °C. A solution of Zn(NO$_3$)$_2$·6H$_2$O (14.9 g, 50 mmol) in water (60 mL) was added dropwise to the well-stirred solution. Then the slightly turbid mixture was added with stirring to distilled water (200 mL) at room temperature, and more water was added until a total volume of 500 mL was reached. The resulting solution (pH ≈ 7) was divided into two equal portions (each of 250 mL). One portion was used as self-assembled ZnWO solution. Concentration of this self-assembled ZnWO solution is about 0.02 mmol ZnWO/mL (assuming a theoretical 100% yield). The other portion of solution was purified according to literature procedure [44], and the isolated Na–ZnWO salt was obtained as needle-like crystals.

The preparation of self-assembled CoWO and the isolated Na–CoWO salt are similar to the ZnWO analogue, with Co(NO$_3$)$_2$·6H$_2$O (14.55 g, 50 mmol) instead of Zn(NO$_3$)$_2$·6H$_2$O. Finally, the self-assembled CoWO solution (pH ≈ 7) of about 0.02 mmol CoWO/mL was obtained.

#### 2.2.2. Self-assembled [WZnMn$_2$(ZnW$_9$O$_{34}$)$_2$]$^{12-}$ (MnZnWO)

The self-assembled MnZnWO was prepared by addition of aqueous Mn(OAc)$_2$ (typically 7.35 g, 30 mmol in 20 mL water) to an aqueous solution of Na–ZnWO (30 g, 5 mmol in 100 mL water). The mixed solution was stirred for 1 h at 60 °C. The precipitate was filtered and divided into two equal portions (each of ~16 g). One portion was added into 125 mL water and used as self-assembled MnZnWO solution (pH ≈ 7). Concentration of this self-assembled MnZnWO solution is about 0.02 mmol MnZnWO/mL (assuming a theoretical 100% yield). The other portion of solution was purified according to literature procedure [44], and the isolated Na–MnZnWO salt was obtained as needle-like crystals.

2.2.3. Self-assembled [PW$_{11}$O$_{39}$]$^{7-}$ (PWO)

The self-assembled PWO was prepared by degradation of Keggin-type H$_3$PW$_{12}$O$_{40}$ with aqueous NaOH. Typically, the aqueous solution of 1 M NaOH was added dropwise to a solution containing 18 g of H$_3$PW$_{12}$O$_{40}$·xH$_2$O (~6 mmol) in 60 mL of distilled water at 50 °C, until the pH value of the mixed solution increased to 5.0. More water was added until a total volume of 120 mL was reached. The resulting solution (pH ≈ 5) was divided into two equal portions (each of 60 mL). One portion was used as self-assembled PWO solution. Concentration of this self-assembled PWO solution is about 0.05 mmol PWO/mL (assuming a theoretical 100% yield). The other portion of solution was evaporated to 10 mL by stirring at 50 °C. Then the resulting solution was refrigerated at 4 °C for 3 days. Finally, the Na–PWO salt was obtained by filtration and dried at 30 °C under vacuum for 24 h.

2.2.4. LDH–NO$_3$ supports

Deionized and decarbonated water was used to prepare all aqueous solution. A solution containing 30 mmol of Mg(NO$_3$)$_2$·6H$_2$O and 10 mmol of Al(NO$_3$)$_3$·9H$_2$O in 100 mL water and an
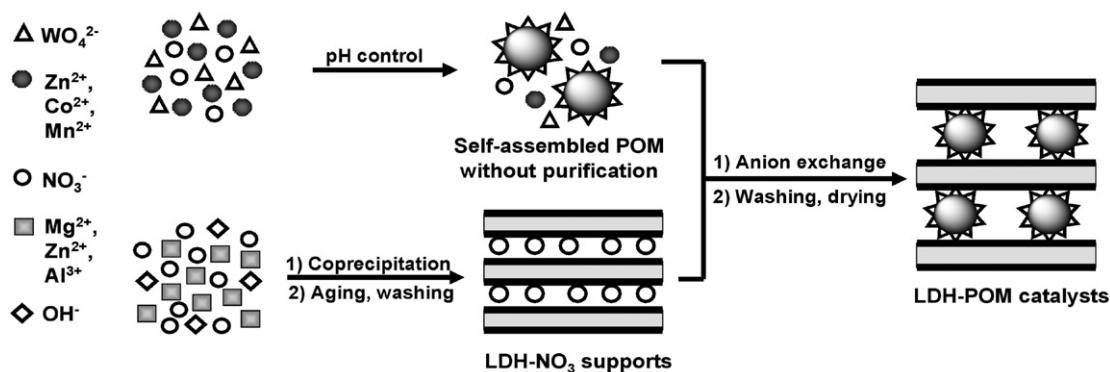
Scheme 1. Schematic representation for the preparation of LDH–POM catalysts using self-assembled POM solutions and LDH–NO$_3$ as precursors.

Table 1
Textural and chemical properties of different LDH–NO$_3$ supports and LDH–POM catalysts.

Sample	d(003) (nm)	S_{BET} (m^2/g)	$S_{microporous}$ (m^2/g)[a]	Composition (Mg:Al:Zn:Mn/P/Co:W)[b]	W loading (wt%)[c]
MgAl–NO$_3$	0.82	7	0	2.93:1.00:–:–:–	–
MgAl–ZnWO	1.49	22	7	2.79:1.00:0.43:–:1.67	41.9
MgAl–MnZnWO	1.52	19	5	2.81:1.00:0.37:0.25:2.33	49.6
MgAl–PWO	1.46	27	3	2.01:1.00:–:0.16:1.77	47.5
ZnAl–NO$_3$	0.89	9	0	–:1.00:2.59:–:–	–
ZnAl–ZnWO	1.53	37	15	–:1.00:2.91:–:1.71	38.6
ZnAl–CoWO	1.51	41	13	–:1.00:2.23:0.43:1.67	39.3
ZnAl–MnZnWO	1.55	33	10	–:1.00:2.85:0.21:2.03	40.2

[a] Determined by t-plot method.
[b] Evaluated by SEM-EDS.
[c] Determined by ICP.

aqueous solution of 1 M NaOH were simultaneously added drop-wise to a 250 mL three-necked flask with rapid stirring under nitrogen atmosphere. The relative rates of adding the mixed solution of nitrate salts and the 1 M NaOH solution were adjusted to maintain the pH $\approx$ 10. More water was added to the slurry until a total volume of 200 mL was reached. After aging at 80 °C for 12 h, the slurry was separated into two equal portions (each of 100 mL). One portion was centrifuged and washed with water for several times, the resulting precipitate was dried at 120 °C overnight and used for characterization. After centrifugation and washing, the other portion of precipitate was dispersed in 100 mL water and maintained under N$_2$ as MgAl–NO$_3$ slurry (pH $\approx$ 7.5). The anion exchange capacity (AEC) of this MgAl–NO$_3$ slurry is about 5 mmol (assuming 10 mmol Al^{3+} all incorporated into LDH layers).

The synthesis of ZnAl–NO$_3$ slurry is similar to the MgAl–NO$_3$ analogue, with Zn(NO$_3$)$_2$·6H$_2$O (30 mmol) instead of Mg(NO$_3$)$_2$·6H$_2$O. The only difference lies in pH control, maintaining the pH $\approx$ 7 during the coprecipitation. Finally, the ZnAl–NO$_3$ slurry (pH $\approx$ 7) with 5 mmol of AEC was obtained.

2.3. Preparation of LDH–POM catalysts

Self-assembled POM anions without isolation and purification were directly used for immobilization. The LDH–POM catalysts were prepared by the procedures as illustrated in Scheme 1 and the data reported in Table 1.

The immobilization of self-assembled ZnWO was done by directly adding a two-fold excess of self-assembled ZnWO solution to the LDH–NO$_3$ slurry. Typically, 42 mL of self-assembled ZnWO solution was added dropwise to the MgAl–NO$_3$ slurry under N$_2$ with rapid stirring. The amount of ZnWO anion (0.84 mmol, $12 \times 0.84 \approx 10$ mmol of negative charge capacity) was two-fold excess of the AEC of the MgAl–NO$_3$ slurry. The mixed slurry (pH $\approx$ 7) was stirred for 3 h at 60 °C. Finally, MgAl–ZnWO catalyst was ob-

tained as a white solid after being washed with boiling water several times and dried at 80 °C for 12 h under vacuum. By the similar procedure, ZnAl–ZnWO, ZnAl–CoWO, MgAl–MnZnWO, and ZnAl–MnZnWO catalysts were also prepared.

The typical procedure for the immobilization of self-assembled PWO was as follows: the MgAl–NO$_3$ slurry (5 mmol of AEC) and 28.6 mL of self-assembled PWO solution (1.43 mmol, $7 \times 1.43 \approx$ 10 mmol of negative charge capacity) were simultaneously added dropwise to a three-necked flask containing 50 mL of decarbonated water with rapid stirring under N$_2$ at 60 °C. While the solution was mixed, a dilute HNO$_3$ solution also was added to maintain the pH $\approx$ 5. After the addition, the resulting slurry was kept stirring at 60 °C for 3 h under N$_2$. Finally, MgAl–PWO catalyst was obtained after being washed with boiling water three times and dried at 80 °C for 12 h under vacuum.

2.4. Epoxidation of allylic alcohols

In a typical experiment, a mixture of prenol (2 mmol), n-dodecane (0.2 mmol, internal standard), aqueous 30% H$_2$O$_2$ (2.4 mmol) and 0.02 mol% of POM species in a vial was magnetically stirred at 50 °C for 10 min under an ambient atmosphere. Then 2 mL of ethyl acetate was added to the reaction mixture. The resulted mixture was cooled by ice bath and stirred for 2 min. After being dried over anhydrous MgSO$_4$, the organic phase was analyzed by GC and GC-MS to determine conversion and selectivity. LDH–POM catalysts were easily recovered by filtration. After being washed with ethyl acetate and dried under vacuum, the recovered catalyst can be reused. Na–POM catalysts were dissolved in aqueous phase and thus cannot be recovered.

2.5. Hydrolysis reaction of epoxide

In a typical run, a reaction mixture of 0.108 g of prenol oxide (95% by GC, 1.0 mmol), n-dodecane (0.1 mmol), 0.1 mL of distilled water or aqueous 30% H$_2$O$_2$ (1.2 mmol), and 0.02 mol% of POM species was stirred at 50 °C for 10 min. Then 2 mL of ethyl acetate was added to the reaction mixture. The resulted mixture was cooled by ice bath and stirred for 2 min. After being dried over anhydrous MgSO$_4$, the organic phase was analyzed by GC to determine the conversion of prenol oxide. Analysis of the organic phase with GC-MS found that triol was the main product.

3. Results and discussion

3.1. Catalyst preparation and characterization

The synthesis route of LDH–POM catalysts is shown in Scheme 1. The self-assembled POM anions without purification were directly used for ion-exchange with LDH–NO$_3$ slurry. To avoid a strong
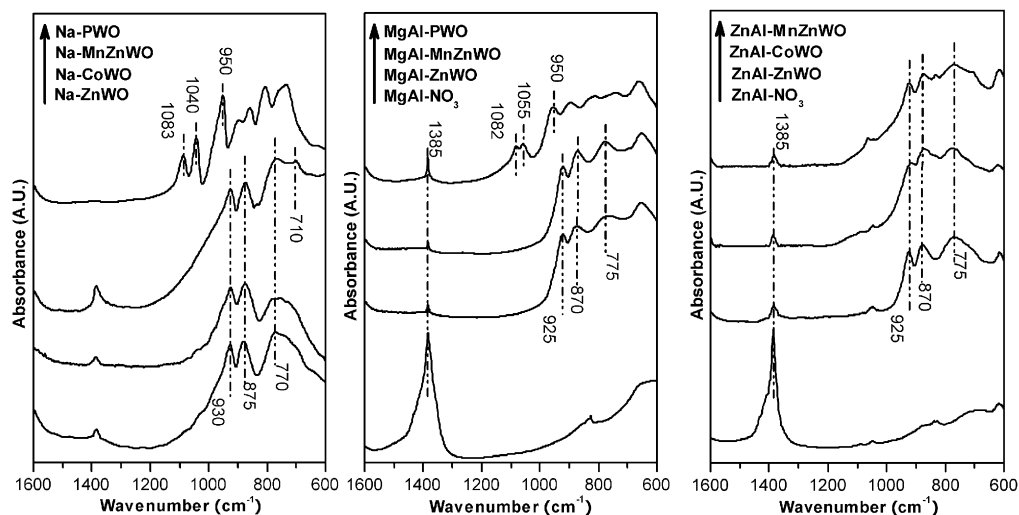
Fig. 1. FT-IR spectra of different Na–POM, LDH–NO$_3$ and LDH–POM samples.
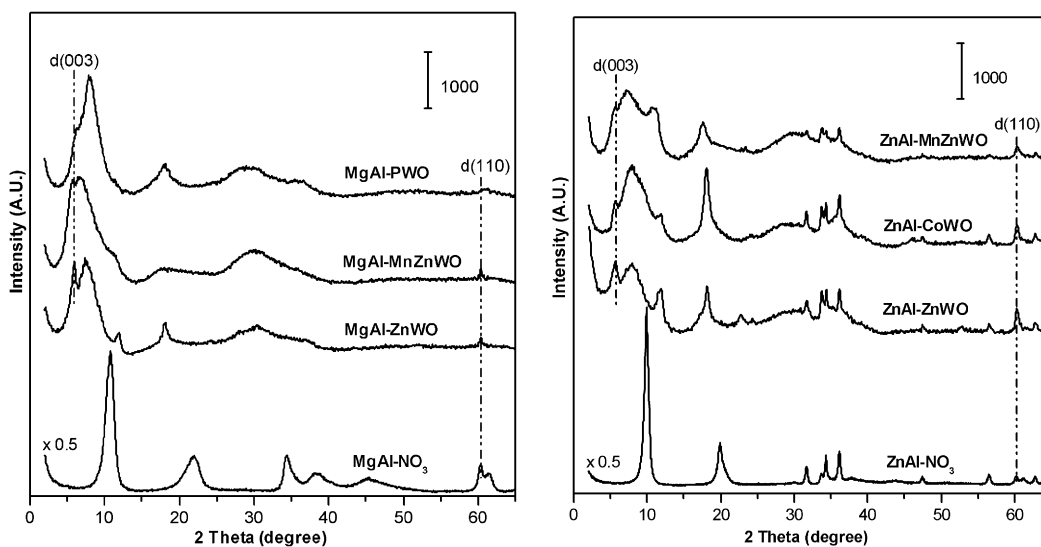

Fig. 2. XRD patterns of different LDH–NO$_3$ supports and LDH–POM catalysts.

acid–base reaction between the acidic POM guest and the basic LDH host, which may cause decomposition of both precursors, the sandwich-type ZnWO, CoWO and MnZnWO were chosen as POM precursors. These POMs were prepared under approximately neutral conditions, and have been demonstrated to be stable even at pH 10 [44]. Thus the self-assembled POM solution (pH $\approx$ 7) can match with the MgAl–NO$_3$ or ZnAl–NO$_3$ slurry (pH $\approx$ 7.5 or 7), and a strict pH controlling is not necessary in the course of anion-exchange.

The direct immobilization method, based on selective exchange of self-assembled POM anion into LDH, was recently used to prepare MgAl–ZnWO catalyst [43]. It allows us to obtain an efficient and recyclable epoxidation catalyst with high dispersion and good hydrothermal stability. In this work, we extended the novel synthesis route to prepare ZnAl–ZnWO, ZnAl–CoWO, MgAl–MnZnWO and ZnAl–MnZnWO catalysts. For comparison, a lacunary Keggin-type PWO was also used for the direct immobilization. Because the PWO is stable at about pH 2–6 [45], the pH value was carefully controlled around 5 to obtain MgAl–PWO catalyst.

FT-IR spectra of the as-prepared samples are presented in Fig. 1. The purified sandwich-type Na–ZnWO, Na–CoWO and Na–MnZnWO exhibit similar characteristic peaks at approximately 930,

875 and 770 cm^{-1}, which are attributed to the vibrations of the W–O$_t$, W–O$_c$–W and W–O$_e$–W (t, terminal; c, corner sharing; e, edge sharing) [20], respectively. In the IR spectrum of the lacunary Keggin-type Na–PWO, the peaks at 1083 and 1040 cm^{-1} are attributed to the vibration of P–O, and the peak at 950 cm^{-1} is attributed to that of W–O$_t$ [45]. The self-assembled POM complexes are a mixture of the desired POM and impurities, as indicated by the IR spectra of the dried samples (not shown) from the self-assembled POM solution [43]. The MgAl–NO$_3$ and ZnAl–NO$_3$ supports show a strong peak at 1385 cm^{-1} due to the vibration of the NO$_3^-$ anion in the interlayer region [30]. The characteristic peaks of Na–POM can be clearly observed in the IR spectrum of LDH–POM with slight shift, whereas the peaks of NO$_3^-$ and other anions are very weak, indicating the prevalence of the desired POM anions, but not of NO$_3^-$ or other anions, in the LDH–POM samples. These results suggest that (a) the self-assembled POM anions were selectively exchanged into LDH supports in the presence of undesired anions, and (b) the structure of POM was retained after the immobilization process.

The powder XRD patterns of various samples are shown in Fig. 2 and the basal d(003) spacings are given in Table 1. The value of the d(003) spacing includes the thickness of the LDH host and
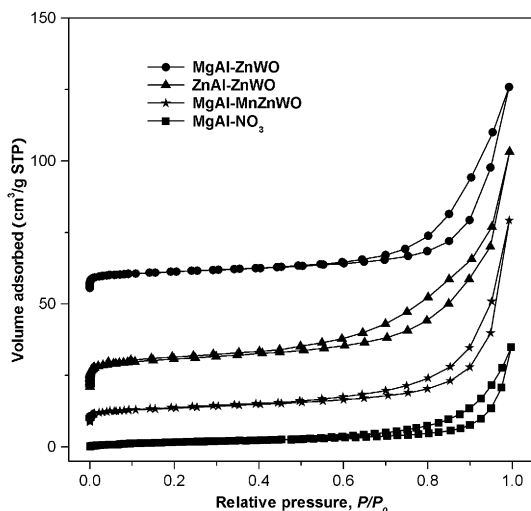
Fig. 3. N$_2$ adsorption–desorption isotherms for the representative LDH–NO$_3$ and LDH–POM samples.

the gallery height of the interlayer region. Subtracting the thickness of the host layer (usually assumed to be about 0.48 nm [31]) from the values of the d(003) spacing of LDH–POM samples give the gallery heights of about 0.98–1.07 nm. These gallery heights are in agreement with the diameter of the short axis of sandwich-type POM anions (dimensions of ∼1.0 to ∼1.5 nm [44]) and that of the Keggin-type PWO (∼1.0 nm [45]). The absence of the reflections of LDH–NO$_3$ and Na–POM (not shown) in the XRD pattern of LDH–POM indicates that the block of LDH–NO$_3$ and Na–POM did not exist in the LDH–POM samples [43]. These results suggest that the self-assembled POM anions have been successfully incorporated into the interlayer of LDH by the anion-exchange process and have a uniform dispersion in the LDH hosts.

A broad diffraction with d-spacing of ∼1.1–1.3 nm was also recorded for all LDH–POM samples, obscuring the peak due to diffraction by the (003) plane. This broad peak has been demonstrated to be rather common in various POM-intercalated LDH materials when recorded in powder form [46], and may be ascribed to the POM anions immobilized on the external surface of the LDH layers. In addition, for all samples, the XRD peak due to diffraction by the (110) plane is always detected at d(110) = 0.153 nm, which is not affected by the size of the interlayer anions [30]. This result indicates that the layered structure of LDH is retained after the immobilization.

Table 1 also summarizes the textural and chemical properties of various samples, and the N$_2$ adsorption–desorption isotherms of the representative samples are shown in Fig. 3. The textural properties of the initial LDH–NO$_3$ are greatly changed upon ion-exchange with self-assembled POM anions. All LDH–POM samples exhibit type I N$_2$ adsorption isotherms at lower relative pressure ($P/P_0 < 0.05$), and H3 type hysteresis loops at higher relative pressure ($P/P_0 > 0.6$), indicating the presence of both interlayer micropores and interparticle mesopores, respectively. About 10–40% of the surface area of LDH–POM samples arises from micropores, whereas no microporous surface area was detected for the LDH–NO$_3$ supports. These results also suggest that the bigger POM anions are incorporated into the interlayer of LDH. The retention of the POM structure in the immobilized form was further confirmed by EDS analysis. The W/Zn, W/Co, W/(Zn + Mn) and W/P atomic ratios calculated from EDS data agree, within experimental error, with the theoretical value of 3.8 for the sandwich-type POMs and that of 11 for the lacunary Keggin-type PWO. Furthermore, in all cases, the contents of W loading determined by ICP are basically in line with the EDS results. The degrees of exchange of POM

into LDH are calculated to be about 103–147%, which are more than the maximum exchange capacity of the LDH supports. This may be ascribed to the unavailability of partial negative charge of POM for balancing the LDH host charge. It is worth noting that the Mg/Al ratio is significantly decreased from 2.93 for MgAl–NO$_3$ to 2.01 for MgAl–PWO. This result indicates that during the synthesis of MgAl–PWO, severe acid–base reaction occurred between the acidic PWO solution and the basic MgAl–NO$_3$, resulting in a partial dissolution of Mg^{2+} ions from the LDH host.

According to the SEM and TEM images in Fig. 4, the well-developed hexagonal plate morphology for LDH host is clearly observed for all LDH–POM samples except for MgAl–PWO. The LDH plate became defective in the TEM image of MgAl–PWO, which may be due to partial decomposition of LDH host under the acidic condition applied in the anion-exchange process. The dark-field TEM image of ZnAl–ZnWO suggests a uniform dispersion of POM nanoclusters (shown as small white dots) throughout the LDH. Furthermore, the ZnWO nanocluster can be directly observed in the HRTEM image of MgAl–ZnWO (see Fig. S1 in Supporting information). The SEM and TEM results are in agreement with the XRD patterns.

The acid–base properties of the representative self-assembled POM, LDH–NO$_3$ and LDH–POM samples are shown in Table 2. While Hammett indicator measurements are conventionally performed using nonpolar solvents [47], it was deemed appropriate to use water/alcohol in this instance, thus allowing a better measure of the sample acid–base strength under reaction conditions where aqueous H$_2$O$_2$ and allylic alcohol are employed as oxidant and reactant, respectively. As expected, although self-assembled ZnWO possesses weak acidity, its solution in water exhibits near neutral pH, thus excluding the possibility of a neutralization reaction between ZnWO and LDH–NO$_3$ during the anion-exchange. For both LDH–NO$_3$ and LDH–ZnWO, the MgAl type LDH has higher surface basicity than the ZnAl type LDH. This fact is in agreement with those from previous reports [32,33].

The foregoing characterization results demonstrate that the LDH supports enable the direct immobilization of a series of self-assembled POM species in the presence of impurities. The effectiveness of this selective immobilization may be attributed to two factors: (a) the desired POM anion has higher negative charge than other anions, and (b) the LDH layer has high positive charge density thus a stronger interaction with the desired POM anion. In addition, sandwich-type POM species were found to be more advantageous than Keggin-type POM for the direct immobilization, primarily due to the compatibility between the sandwich-type POM and the basic LDH supports, which can avoid the strict pH controlling and keep the LDH host intact during the anion-exchange process.

3.2. Catalytic performance in the epoxidation of prenol with aqueous H$_2$O$_2$

The epoxidation of prenol with aqueous 30% H$_2$O$_2$ was chosen as the model reaction to evaluate the catalytic performance of the different catalysts (Scheme 2). This reaction was performed with 0.02 mol% of POM species and 1.2 equivalence of H$_2$O$_2$ at 50 °C under organic solvent-free conditions to meet the requirement of green epoxidation, because H$_2$O$_2$ can be a clean oxidant only if it is used in a controlled manner without organic solvents and other toxic compounds [48].

3.2.1. Effect of the nature of the POM species

Catalytic performance in prenol epoxidation differed greatly between Na–POM catalysts and LDH–POM catalysts (Table 3). All Na–POM catalysts gave high prenol conversion (>90%) but low selectivity (<30%) of epoxide (entries 1–4). Epoxide hydrolysis is the
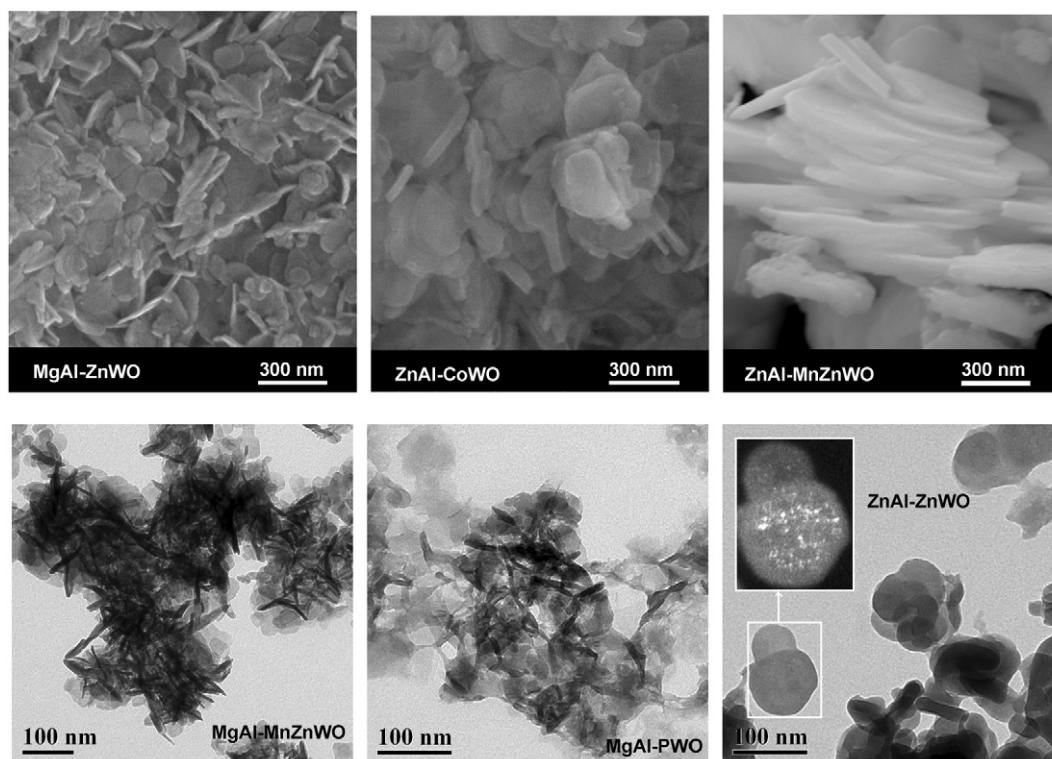
Fig. 4. SEM and TEM images of different LDH–POM catalysts.

Table 2

Characterization of acid–base properties of the representative self-assembled POM, LDH–NO$_3$ and LDH–POM samples.

Sample	pH value of suspension in		Acid/base strength[c]	Basic sites (μmol g^{-1})[d]
	H$_2$O[a]	pH 2 HNO$_3$[b]		
Self-assembled ZnWO[e]	7.1	3.6	$6.0 < H_0 < 7.2$	–
MgAl–NO$_3$	8.3	5.9	$H_- > 9.3$	560
ZnAl–NO$_3$	7.5	4.8	$8.1 < H_- < 8.8$	320
MgAl–ZnWO	7.8	5.6	$7.2 < H_- < 8.1$	380
ZnAl–ZnWO	7.2	5.1	$7.2 < H_- < 8.1$	250
MgAl–ZnWO-re[f]	7.3	5.2	$7.2 < H_- < 8.1$	270

  [a] Suspension of 0.1 g solid sample in 10 mL distilled H$_2$O.
  [b] Suspension of 0.1 g solid sample in 10 mL dilute HNO$_3$ solution with pH 2.
  [c] Measured by Hammett indicator.
  [d] 0.05 g dried sample, suspended in 2 mL indicator (bromothymol blue, pK_a = 7.2) solution (0.1 mg/mL), is titrated with 0.01 M benzoic acid.
  [e] Dried sample from self-assembled ZnWO solution.
  [f] Recovered MgAl–ZnWO catalyst after the fifth recycling.
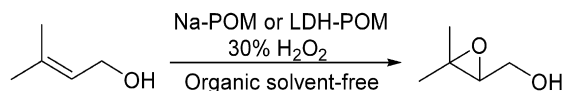
Scheme 2. Epoxidation of prenol with aqueous H$_2$O$_2$.

major side-reaction in the homogeneous epoxidation as indicated by GC-MS. On the other hand, LDH–POM catalysts exhibit comparable reactivity to and much higher selectivity (81–98%) than those of Na–POM catalysts under identical conditions (entries 5–10), indicating an effective suppression of epoxide hydrolysis in the heterogeneous epoxidation. This significant selectivity enhancement is mainly due to the effect of the LDH host, which will be discussed in the next section. In addition, epoxidation of prenol with both Na–ZnWO and MgAl–ZnWO catalysts starts without an induction period (see Fig. S2 in Supporting information), which is in accordance with previous reports [25].

Table 3

Epoxidation of prenol on different catalysts with aqueous 30% H$_2$O$_2$ under organic solvent-free conditions.[a]

Entry	Catalyst	Conv. (%)		Selec.[b] (%)	H$_2$O$_2$ eff.[d] (%)
		Prenol[b]	H$_2$O$_2$[c]		
1	Na–ZnWO	98	88	27	25
2	Na–CoWO	92	98	15	12
3	Na–MnZnWO	96	92	23	20
4	Na–PWO	95	90	25	22
5	MgAl–ZnWO	95	82	98	95
6	ZnAl–ZnWO	95	83	93	89
7	ZnAl–CoWO	85	95	81	60
8	MgAl–MnZnWO	90	88	97	83
9	ZnAl–MnZnWO	89	87	92	78
10	MgAl–PWO	91	85	93	83

  [a] Reaction conditions: 2 mmol prenol, 2.4 mmol of aqueous H$_2$O$_2$, 0.02 mol% of POM, 0.2 mmol *n*-dodecane, 50 °C, 10 min.
  [b] Prenol conversion and epoxide selectivity were determined by GC with an internal standard technique.
  [c] H$_2$O$_2$ conversion was determined by cerimetry.
  [d] H$_2$O$_2$ efficiency was calculated as mole of epoxide produced per mole of H$_2$O$_2$ consumed.

The H$_2$O$_2$ efficiency (defined as mole of epoxide produced per mole of H$_2$O$_2$ consumed) represents another important issue in liquid phase epoxidation. Side-reaction (such as epoxide hydrolysis) and unproductive decomposition of H$_2$O$_2$ can decrease the H$_2$O$_2$ efficiency. Interestingly, for both homogeneous Na–POM catalysts and heterogeneous LDH–POM catalysts, the H$_2$O$_2$ efficiency is increased in the order CoWO < MnZnWO < PWO < ZnWO, indicating that the ZnWO species show relatively slower decomposition of H$_2$O$_2$ than other POM species. This result is similar to the findings reported by Sloboda-Rozner et al. [49]. The excessive decomposition of H$_2$O$_2$ may be the major reason for the lower conversion of the CoWO catalysts (entries 2 and 7), because only 1.2 equivalence of H$_2$O$_2$ was used as oxidant. Furthermore, since the decomposition of H$_2$O$_2$ is an exothermic process, the resulting higher local temperature may cause the lower epoxide selectivity of the CoWO

Table 4
The effect of different base additives on the epoxidation of prenol.[a]

Entry	Catalyst	Additives	Conv. (%)		Selec.[b] (%)	H$_2$O$_2$ eff.[d] (%)
			Prenol[b]	H$_2$O$_2$[c]		
1	Na–ZnWO	–	98	88	27	25
2	Na–ZnWO	Pyridine[e]	86	98	85	62
3	Na–ZnWO	MgAl–NO$_3$[f]	75	63	86	85
4	Na–ZnWO	ZnAl–NO$_3$[f]	81	68	83	82
5	MgAl–ZnWO	–	95	82	98	95
6	MgAl–ZnWO	Pyridine[e]	83	98	95	67
7	ZnAl–ZnWO	–	95	83	93	89
8	ZnAl–ZnWO	Pyridine[e]	80	98	91	62

[a] Reaction conditions: 2 mmol prenol, 2.4 mmol of aqueous H$_2$O$_2$, 0.02 mol% of ZnWO, 0.2 mmol *n*-dodecane, 50 °C, 10 min.
[b] Prenol conversion and epoxide selectivity were determined by GC with an internal standard technique.
[c] H$_2$O$_2$ conversion was determined by cerimetry.
[d] H$_2$O$_2$ efficiency was calculated as mole of epoxide produced per mole of H$_2$O$_2$ consumed.
[e] Pyridine: 0.2 mmol.
[f] LDH–NO$_3$: 1.0 mg.

catalysts. Comparing the findings for different LDH–POM catalysts reveals a higher selectivity to epoxide (up to 98%) and H$_2$O$_2$ efficiency (up to 95%) for MgAl–ZnWO catalyst (entry 5), indicating that the MgAl–ZnWO catalyst is more favorable for the epoxidation.

3.2.2. Effect of the LDH host and other base additives

The results in Table 3 also suggest that there is a positive effect of LDH host on the aqueous H$_2$O$_2$-based epoxidation, because the LDH–POM catalyst shows superior epoxide selectivity to the corresponding Na–POM catalyst. Moreover, MgAl–ZnWO shows a higher selectivity of epoxide (98%) than that of ZnAl–ZnWO (93%). The same trend was also observed for MgAl–MnZnWO (97%) and ZnAl–MnZnWO (92%). These results suggest that the MgAl type LDH host is more effective for improving the epoxide selectivity. The major difference between the MgAl and the ZnAl type LDH hosts lies in their surface basicity: the MgAl type LDH has stronger surface basicity than the ZnAl type LDH, thus implying that the enhanced epoxide selectivity is related to the basicity of LDH hosts.

To understand the effect of basic LDH on the catalytic performance of POM species, further epoxidation tests were conducted on Na–ZnWO and LDH–ZnWO samples with other base additives (Table 4). The addition of pyridine to the homogeneous system was found to enhance the epoxide selectivity evidently (from 27 to 85%, entry 2), which can be due to the buffer effect of basic pyridine for suppression of the acid-catalyzed epoxide hydrolysis and this is consistent with those reported for other POM-catalyzed epoxidations [8–10,23]. Although it has been demonstrated that LDH can be used as solid base catalyst for the epoxidation [32], control experiments performed with MgAl–NO$_3$ or ZnAl–NO$_3$ alone showed negligible activity (<5% conversion for both prenol and H$_2$O$_2$ after 10 min, results not listed). The physical mixture of LDH–NO$_3$ supports and Na–ZnWO catalyst (entries 3 and 4), in which LDH–NO$_3$ was directly used as base additives, showed relatively lower selectivity and activity than the corresponding LDH–ZnWO catalysts. It is worth noting that LDH–ZnWO catalysts gave lower prenol conversion and higher H$_2$O$_2$ conversion in the presence of pyridine (entries 6 and 8) than those obtained in the absence of pyridine (entries 5 and 7), indicating that pyridine decomposed H$_2$O$_2$ nonproductively and led to low H$_2$O$_2$ efficiency. These findings suggest that the LDH hosts play crucial roles in the reaction: (a) they disperse ZnWO species thoroughly, which leads to high activity, and (b) they are more effective than pyridine to act as base additives to suppress the acid-catalyzed hydrolysis of epoxide and to give high epoxide selectivity and high H$_2$O$_2$ efficiency.

Table 5
Comparison of hydrolysis of prenol oxide with water and with aqueous 30% H$_2$O$_2$ in the presence of different ZnWO samples.[a]
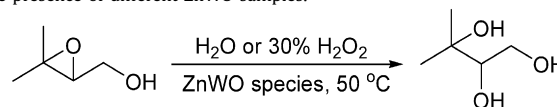
ZnWO sample	With water		With 30% H$_2$O$_2$		
	Time (h)	Conv. of oxide (%)[b]	Time (min)	Conv. of oxide (%)[b]	Conv. of H$_2$O$_2$ (%)[c]
None	2	4	10	93	2
Na–ZnWO	2	5	10	89	5
MgAl–ZnWO	2	2	10	7	4
ZnAl–ZnWO	2	3	10	13	3

[a] Reaction conditions: 1 mmol prenol oxide, 0.1 mL distilled water or 0.1 mL (1.2 mmol) of aqueous 30% H$_2$O$_2$, 0.02 mol% of ZnWO, 0.1 mmol *n*-dodecane, 50 °C.
[b] Conversion of prenol oxide was determined by GC with an internal standard technique.
[c] H$_2$O$_2$ conversion was determined by cerimetry.

3.2.3. Epoxide hydrolysis reaction

To gain further insight into the role of basic LDH hosts played in suppressing the acid-catalyzed hydrolysis of epoxide, we investigated the hydrolysis reaction of prenol oxide in the presence of Na–ZnWO and LDH–ZnWO samples. It is known that both the POM species and aqueous H$_2$O$_2$ possess acidity, but it is not clear that whose acidity really cause the hydrolysis of epoxide. Thus, the hydrolysis of prenol oxide was investigated under two conditions: the hydrolysis with pure water for 2 h, and the hydrolysis with aqueous H$_2$O$_2$ for 10 min (Table 5). The main product was 3-methyl-butane-1,2,3-triol, along with a few products of high boiling points. Slow hydrolysis rate was observed in the former case, even in the presence of Na–ZnWO (5% conversion after 2 h), indicating that the acidity of ZnWO species is not strong enough to cause the epoxide hydrolysis. In the latter case, aqueous H$_2$O$_2$ considerably accelerated the epoxide hydrolysis in the absence of ZnWO species (93% conversion after 10 min) and in the presence of Na–ZnWO (89% conversion), but an effective slowdown of the hydrolysis (conversion <15%) was observed in the presence of LDH–ZnWO. It should be pointed out that the conversion of H$_2$O$_2$ was very low (<6%) in all cases. These results suggest that (a) the acid-catalyzed epoxide hydrolysis is owing to the acidity of aqueous H$_2$O$_2$, (b) the hydrolysis mainly occurs in solution rather than on the surface of ZnWO, and (c) the origin of the beneficial effect of basic LDH hosts is related to the suppression of the acidity of aqueous H$_2$O$_2$.

3.2.4. Effect of the pH value of aqueous H$_2$O$_2$

Because H$_2$O$_2$ solution is more stable in acid medium, commercial aqueous H$_2$O$_2$ solutions (30–70%) are generally stabilized at a pH of 1–4. In our experiments, the pH value of aqueous 30% H$_2$O$_2$ was determined to be 2.5. To further affirm the influence of the acidity of aqueous H$_2$O$_2$ on the epoxidation of prenol, a series of H$_2$O$_2$ solutions with varying pH value were prepared by using dilute nitric acid and sodium hydroxide solutions (Table 6). With increasing the pH value of aqueous H$_2$O$_2$ from 1.5 to 5.3, the prenol conversion is decreased gradually for both Na–ZnWO and MgAl–ZnWO catalysts, and the H$_2$O$_2$ efficiency is decreased obviously for MgAl–ZnWO, due primarily to the faster decomposition of H$_2$O$_2$ at higher pH values. The epoxide selectivity of Na–ZnWO catalyst increases steadily from 12 to 82% with decreasing the amount of protonic acid in aqueous H$_2$O$_2$, indicating that the pH controlling is necessary to improve the catalytic selectivity for homogeneous epoxidation. This finding is consistent with the results of previous reports [7,11]. Notably, the epoxide selectivity of MgAl–ZnWO catalyst can retain over 95% even when the pH value of aqueous H$_2$O$_2$ is decreased to 1.5, implying that the LDH host can buffer the acidity of aqueous H$_2$O$_2$ and protect the epoxide from hydrolysis.

Table 6
The effect of pH value of aqueous H_2O_2 on the epoxidation of prenol.[a]

pH value[b]	Na–ZnWO				MgAl–ZnWO			
	Conv.[c] (%)	Selec.[c] (%)	H_2O_2 (%)		Conv.[c] (%)	Selec.[c] (%)	H_2O_2 (%)	
			Conv.[d]	Eff.[e]			Conv.[d]	Eff.[e]
1.5	99	12	87	11	96	95	81	94
2.5	98	27	88	25	95	98	82	95
3.3	95	53	90	47	93	98	85	89
4.5	90	69	95	54	89	98	90	81
5.3	86	82	98	60	85	96	96	71

[a] Reaction conditions: 2 mmol prenol, 2.4 mmol of aqueous H_2O_2, 0.02 mol% of ZnWO, 0.2 mmol n-dodecane, 50 °C, 10 min.

[b] Aqueous H_2O_2 solutions with different pH value were prepared by using dilute nitric acid and sodium hydroxide solutions.

[c] Prenol conversion and epoxide selectivity were determined by GC with an internal standard technique.

[d] H_2O_2 conversion was determined by cerimetry.

[e] H_2O_2 efficiency was calculated as mole of epoxide produced per mole of H_2O_2 consumed.

One possible mechanism for the "buffer effect" of LDH is that the surface hydroxyl groups of LDH host may act as base sites to trap the protonic acid in aqueous H_2O_2, thus reducing the possibility for the acid-catalyzed epoxide hydrolysis in solution. This can explain the fact that the epoxide selectivity of MgAl–PWO catalyst (93%) was lower than that of MgAl–ZnWO or MgAl–MnZnWO catalyst in the presence of aqueous H_2O_2 with a pH of 2.5 (Table 3), because the LDH host of MgAl–PWO has been partially decomposed during catalyst synthesis as mentioned above. Therefore, we found that the cooperation of the POM guest and the LDH host on LDH–POM catalysts can realize a significant selectivity enhancement in the epoxidation without the need for any added base additives or pH controlling. The success of this cooperation effect can be ascribed to the selection of sandwich-type POM precursors, which are compatible with the basic LDH supports and do not need strict pH controlling during immobilization thus keeping the LDH host intact.

Most previous publications on LDH–POM catalysts for epoxidation reaction have focused on the acid-stable POM species, which need acidic condition (pH < 5) during the immobilization process to protect the POM from degradation [34–36,38,40]. However, under such conditions, the LDH supports would be decomposed inevitably, and the role of LDH could not be evaluated authentically. In addition, due to the hydrolytic instability of the acid-stable POM species, anhydrous H_2O_2 in organic solvent was often used as oxidant [34–39], and the acidity of H_2O_2 solution has often been ignored. Although some reports have described the correlation between epoxide selectivity and LDH host, the role of LDH was unclear. For example, Gardner and Pinnavaia [36] reported that the surface acid–base properties of the LDH may promote ring opening of the epoxide to the diol; and Watanabe et al. [35] suggested that the hydrolysis of epoxide mainly occurred on POM sites which located at the outer surface of LDH host. However, the results in this report undoubtedly confirm that the basic LDH host can suppress the acidity of aqueous H_2O_2 and improve the epoxide selectivity without apparent loss of H_2O_2 efficiency. Namely, our findings demonstrate the origin of the beneficial effect of LDH–POM catalysts on the aqueous H_2O_2-based epoxidation.

3.2.5. Stability and reusability of LDH–POM catalysts

In order to obtain the information on the stability of POM species in the LDH matrix, MgAl–ZnWO, MgAl–MnZnWO and MgAl–PWO catalysts were recycled in the epoxidation of prenol (Fig. 5). The solid catalysts could be readily separated from the reaction mixture by filtration. To our delight, MgAl–ZnWO and MgAl–MnZnWO could be recycled and reused at least five times without apparent loss of activity and selectivity, and the epoxide
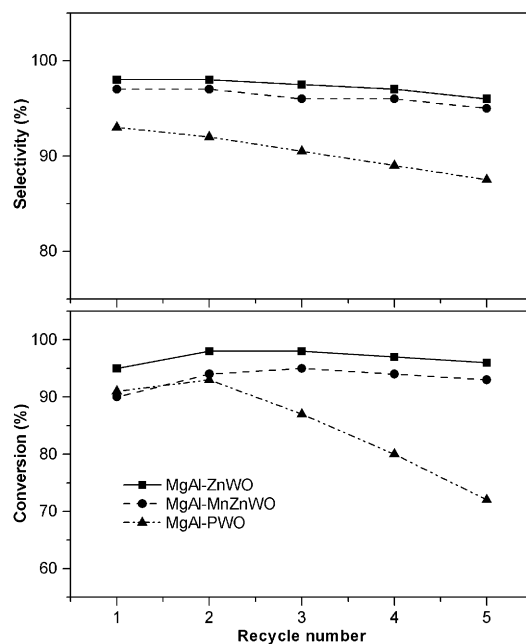

Fig. 5. Reusability of MgAl–ZnWO, MgAl–MnZnWO and MgAl–PWO catalysts. Reaction conditions: 2 mmol prenol, 2.4 mmol of aqueous H_2O_2, 0.2 mmol n-dodecane, 50 °C, 10 min; for the first cycle, 0.02 mol% of POM species were added.

selectivity retained over 95% even after the five-time use. However, the activity of the MgAl–PWO catalyst is decreased after the first reuse, suggesting that the PWO species is unstable toward the epoxidation. ICP analysis of the filtrate shows that 6% of the W (relative to the total W content) had leached from MgAl–PWO during the first cycle of epoxidation. This can be explained by the fact that the PWO anion can decompose into the smaller peroxo-POM anions in the presence of aqueous H_2O_2 [45]. These smaller POM anions may leach from the LDH–POM gradually during the epoxidation, because they have lower negative charge and thus have weak interaction with the LDH host. On the contrary, for MgAl–ZnWO and MgAl–MnZnWO catalysts, no leaching of W species after the first cycle was detected; and when the catalysts were removed from the reaction mixture after 5 min at about 60% conversion of the prenol, no further epoxidation was detected in the filtrate even after 1 h with added aqueous H_2O_2. These results demonstrate that MgAl–ZnWO and MgAl–MnZnWO are stable heterogeneous catalysts in the aqueous epoxidations.

The recovered MgAl–ZnWO catalyst after the fifth cycle was characterized again by EDS, FT-IR and UV-Raman to evaluate the structural stability. Compared to the fresh catalyst, the W/Zn ratio retained 3.8 and the Mg/Al ratio decreased from 2.79 to 2.63, indicating that part of MgAl LDH host decomposed along with the successive recycling. This can be ascribed to the acid–base reaction between aqueous H_2O_2 and LDH host, which reduce the amount of basic sites in the recovered MgAl–ZnWO catalyst as indicated in Table 2. Therefore, the decreasing surface basicity of MgAl–ZnWO catalyst is the reason why slightly lower epoxide selectivity (96%) was obtained for the fifth cycle of the epoxidation.

UV-Raman spectra in Fig. 6 show three Raman bands at 956, 880 and 790 cm^{-1} for Na–ZnWO sample, and these bands can be assigned to the $\nu(W-O_t)$, $\nu(W-O_c-W)$ and $\nu(W-O_e-W)$, respectively. It is very interesting to note that the intensity of the band at 956 cm^{-1} is enhanced after the ZnWO is incorporated into LDH, which may be due to the better disperse of ZnWO on LDH. No significant changes in the Raman spectra and IR spectra (not shown) were observed for the recovered MgAl–ZnWO catalyst. This fact
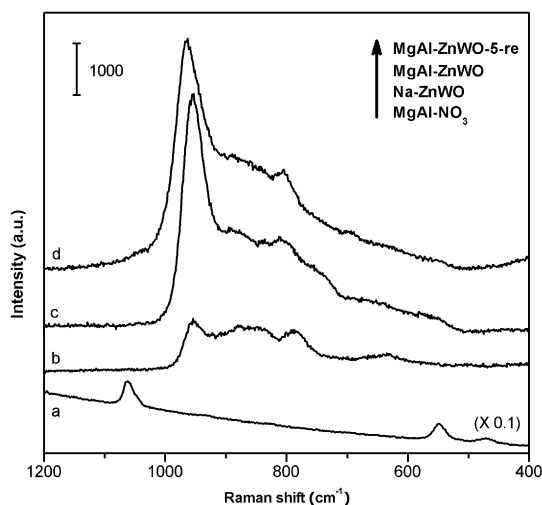
Fig. 6. UV-Raman spectra of representative samples: (a) MgAl–NO$_3$ support, (b) Na–ZnWO catalyst, (c) fresh MgAl–ZnWO catalyst, and (d) recovered MgAl–ZnWO catalyst after the fifth recycling.

provides direct evidence that the ZnWO species in MgAl–ZnWO catalyst is stable under the reaction conditions.

### 3.3. Epoxidation of other allylic alcohols

To extend the substrate scope for the heterogeneous catalytic epoxidation, the epoxidation of various allylic alcohols with 1.2 equivalence of aqueous H$_2$O$_2$ was carried out under organic solvent-free conditions. As listed in Table 7, the MgAl–ZnWO catalyst (method B) successfully suppressed the hydrolysis of epoxide and showed high selectivities (up to 99%) for the epoxidation of

various allylic alcohols. Although homogeneous Na–ZnWO catalyst (method A) gives relatively higher conversions, the selectivities are much lower. This once and again verifies the beneficial effect of LDH host on the selectivity. Epoxidation of water miscible allylic alcohols (entries 1–3) shows turnover frequency (TOF) of more than 3000 h^{-1}. Prenol is more active than butenol and pentenol, mainly due to the higher nucleophilicity of the C=C. However, since epoxidation is an exothermic reaction, the high initial rate of homogeneous epoxidation of prenol (see Fig. S2 in Supporting information) may release more heat thus accelerating the epoxide hydrolysis. Significantly, for heterogeneous epoxidation of prenol, excellent catalytic activity and selectivity are achieved even at very low catalyst loading of only 0.005 mol% (entry 2), which illustrates unequivocally the high efficiency (TOF up to 37200 h^{-1}) of MgAl–ZnWO catalyst. Interestingly, for homoallylic alcohol (entry 4), high selectivity to epoxidation (98%) can also be obtained by using MgAl–ZnWO catalyst. For the epoxidation of more hydrophobic allylic alcohols (entries 5–7), relatively lower TOF values were obtained owing to the hydrophilic nature of Na–ZnWO and LDH–ZnW.O The regioselective epoxidation of geraniol (entry 7) proceeded smoothly in the solvent-free heterogeneous system to give 2,3-epoxy alcohol by a TOF of 580 h^{-1}; with addition of acetonitrile solvent, high efficiency (TOF ~2710 h^{-1}) could also be achieved.

To the best of our knowledge, the MgAl–ZnWO is one of the most efficient, environmentally benign POM catalyst for the epoxidation of allylic alcohols in the liquid phase with the advantages of (1) high catalytic activity, even with about stoichiometric amount of aqueous H$_2$O$_2$ as the oxidant, (2) effective suppression of epoxide hydrolysis in the absence of additional base additives and pH controlling, (3) mild and organic solvent-free conditions, (4) simple preparation and work-up procedures, and (5) reusability as a heterogeneous catalyst. The excellent activity and reusability of this type of catalyst shows a great potential for practical applications.

Table 7
Catalytic epoxidation of various allylic alcohols with aqueous 30% H$_2$O$_2$ under organic solvent-free conditions.[a]
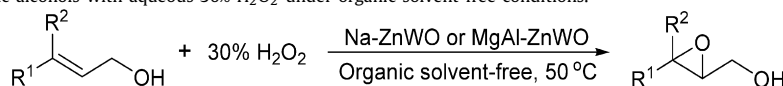
Entry	Allylic alcohol	Method[b]	Time (h)	Conv.[c] (%)	Selec.[c] (%)	TOF[d] (h^{-1})
1[e]		A	0.25	99	90	7120
		B	0.25	93	98	7290
2[f]		A	0.5	96	27	10360
		B	0.5	95	98	37200
3		A	0.5	95	91	3450
		B	0.5	81	99	3200
4		A	2	60	15	160
		B	2	57	98	980
5		A	1	91	90	2260
		B	1.5	93	99	1660
6		A	1.5	98	90	1470
		B	2.5	90	99	1180
7		A	2	72	90	1150
		B	2	42	97	580
		B[g]	1	96	97	2710

[a] Reaction conditions: 2 mmol substrate, 2.4 mmol aqueous H$_2$O$_2$, 0.05 mol% of ZnWO, 0.2 mmol n-dodecane, 50 °C.
[b] Method A: homogeneous epoxidation with Na–ZnWO; method B: heterogeneous epoxidation with MgAl–ZnWO.
[c] Conversions and selectivities were determined by GC and GC-MS using n-dodecane as internal standard.
[d] Based on the epoxide yield after 0.5 h, and given in mmole of epoxide produced per mmole of ZnWO in the catalyst per hour.
[e] Substrate: $cis/trans$ = 5:95, product: $cis/trans$ = 5:95; TOF value was based on the epoxide yield after 0.25 h.
[f] 10 mmol prenol, 12 mmol aqueous H$_2$O$_2$, 0.005 mol% of ZnWO, 1 mmol n-dodecane, 50 °C.
[g] Added 0.2 mL acetonitrile.

4. Conclusions

In summary, we have described a convenient, time- and cost-saving procedure for the incorporation of POM guests into LDH hosts to afford efficient heterogeneous epoxidation catalysts. Using self-assembled POM solutions as precursors, the desired POM can be selectively ion-exchanged into LDH supports even in the presence of other anions. Sandwich-type POM species are more advantageous than Keggin-type POM for the direct immobilization process, because strict pH controlling is not needed and the LDH host can be kept intact. The catalytic performance of the LDH–POM catalysts in organic solvent-free epoxidation with aqueous H_2O_2 strongly depends on the type of POM, the surface basicity of LDH, the pH value of aqueous H_2O_2, and the hydrophilicity of substrate. MgAl–ZnWO catalyst shows up to 99% epoxide selectivity, 95% H_2O_2 efficiency and 37200 h^{-1} TOF without the need of any added base additives and pH controlling for the epoxidation of allylic alcohols. The LDH–POM catalyst shows much higher epoxide selectivity than the corresponding homogeneous Na–POM catalyst, which has been attributed to the beneficial effect of basic LDH host on suppression of the acid-catalyzed epoxide hydrolysis. The MgAl type LDH host with higher surface basicity is more effective than the ZnAl type LDH to improve the epoxide selectivity by suppressing the acidity of aqueous H_2O_2. The sandwich-type ZnWO and MnZnWO species show higher stability than the lacunary Keggin-type PWO toward recycling, and the LDH-hosted (Mn)ZnWO catalysts can be readily recovered and reused with no apparent loss of performance. This cooperation between POM guests and LDH hosts offers a green chemistry strategy for selectivity improvement of heterogeneous epoxidation using aqueous H_2O_2.

Acknowledgments

Supporting information

Supporting information for this article may be found on ScienceDirect, in the online version.
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