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Research Note

# Direct immobilization of self-assembled polyoxometalate catalyst in layered double hydroxide for heterogeneous epoxidation of olefins

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ABSTRACT

We present a novel method for the fabrication of immobilized polyoxometalate catalysts that directly use a self-assembled polyoxometalate solution without isolation and purification. Specifically, self-assembled $[WZn_3(ZnW_9O_{34})_2]^{12-}$ catalyst can be selectively immobilized into layered double hydroxides in the presence of undesired anions. The material thus obtained demonstrates high dispersion and good hydrothermal stability. The heterogenized catalyst exhibits excellent activity (turnover frequency up to 18,000 $h^{-1}$ at 50 °C) in the epoxidation of allylic alcohols with aqueous $H_2O_2$ and can be readily recycled with no apparent loss of performance.

## 1. Introduction

Recently, considerable attention has been devoted to the immobilization of olefin epoxidation catalysts onto solid supports to increase catalyst stability and allow for catalyst recovery and product separation [1,2]. Among the various homogeneous epoxidation catalysts, polyoxometalates (POM) are promising due to their oxidative stability and high efficiency [3–5]. However, tedious procedures are often needed to prepare such heterogenized POM catalysts [6–8], and common problems include slow reaction rates and reduced catalytic activity/selectivity upon reuse. The development of a facile, efficient method for the immobilization of POM catalysts remains a challenge.

Interest is growing in the applications of self-assembled POM solution for homogeneous oxidation [9–14]. Compared with the purified POM salts commonly used as catalysts, self-assembled POM has the advantage of high availability and cost efficiency, because tedious POM isolation and purification are not required. This offers the possibility of immobilizing POM in a facile way without the typically long synthesis time. However, direct immobilization of self-assembled POM has not been achieved, because the state of most POMs in solution is generally complicated, particularly at different pH values [3]. Herein we present the first example of the immobilization of self-assembled $[WZn_3(ZnW_9O_{34})_2]^{12-}$ (ZnWO) catalyst into layered double hydroxides (LDHs). The efficiency of this novel approach is based on the anion-exchange capability and high positive charge density of LDH host [15–17], which may benefit the selective immobilization of ZnWO polyanion in the presence of other anions. The material thus obtained, LDH-ZnWO, exhibits high dispersion and good hydrothermal stability and can be used as a highly active and recyclable catalyst for the epoxidation of allylic alcohols with aqueous $H_2O_2$.

## 2. Experimental

The self-assembled ZnWO solution was prepared by gradual addition of aqueous $Zn(NO_3)_2$ to an aqueous solution of $Na_2WO_4$ and nitric acid with a molar ratio of $Zn(NO_3)_2/Na_2WO_4/HNO_3 = 5/19/16$ [10]. After purification, Na-ZnWO salt also was obtained as needle-like crystals [18]. The LDH-$NO_3$ support was prepared by co-precipitation of mixed metal nitrates ($Mg^{2+}/Al^{3+} = 3/1$) with base (1 M NaOH) from aqueous solutions at pH $\approx$ 10 under $N_2$ [15]. After aging at 80 °C for 12 h, the precipitate was centrifugated and washed several times with water; a portion of the precipitate was dried and used for characterization, whereas the remaining portion was dispersed in water and maintained under $N_2$ as LDH slurry. The immobilization of self-assembled ZnWO was done by directly adding a two-fold excess of self-assembled ZnWO solution to the LDH slurry (see Supporting information for details). The mixed slurry (pH $\approx$ 7.5) was then stirred for 3 h at 60 °C under $N_2$. Finally, the LDH-ZnWO catalyst was obtained as a white solid after centrifugation, washing, and drying.

FTIR spectra were collected on a Thermo-Nicolet Nexus 470 infrared spectrometer using KBr pallet method. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 3400 powder diffraction system (Cu*Kα*, 40 kV, 100 mA). TEM micrographs were

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obtained with a JEOL JEM-2000EX transmission electron microscope at an acceleration voltage of 120 kV. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis was performed on Leeman Plasma-spec-II spectrometer. Thermogravimetric analysis (TGA) was carried out in air on a Perkin Elmer Pyris Diamond TG instrument in a range of 20–800 °C at a heating rate of 5 °C/min.

Epoxidation reactions were carried out in acetonitrile ($CH_3CN$) at 50 °C with aqueous 30% $H_2O_2$ as the oxidant and *n*-dodecane as the internal standard. Qualitative analysis of the reaction products was performed on an Agilent 6890N GC/5973 MS detector. Quantitive analysis was performed on an Agilent 6890N GC with an HP-19091G-B213 capillary column. The LDH-ZnWO catalyst was readily recovered by filtration. After being washed with ethyl acetate, the recovered catalyst was used in the recycling experiments. Details of the epoxidation tests are given in Supporting information.

## 3. Results and discussion

FTIR spectra of the various samples are shown in Fig. 1. The LDH-$NO_3$ support exhibited a very strong peak at 1385 $cm^{-1}$ due to the vibration of the $NO_3^-$ anion in the interlayer region [15]. In the IR spectrum of the dried sample from the self-assembled ZnWO solution, three peaks at approximately 930, 875 and 770 $cm^{-1}$ are assigned to the ZnWO species [6,9], consistent with the spectrum of the purified Na-ZnWO salt (Fig. 1d). Furthermore, the strong peak of $NO_3^-$ at 1385 $cm^{-1}$ is attributed to the high amount of nitrate, and the peak at 835 $cm^{-1}$ is attributed to the vibration of the $WO_4^{2-}$. Thus, the self-assembled ZnWO solution is a real mixture of nitrate coproduct, unreacted tungstate, and desired ZnWO. To our delight, the characteristic peaks of ZnWO could be clearly observed in the IR spectrum of LDH-ZnWO, whereas the peaks of $NO_3^-$ and $WO_4^{2-}$ were very weak, indicating the prevalence of the ZnWO anion, but not of $NO_3^-$ or $WO_4^{2-}$, in the LDH-ZnWO. These results suggest that (a) the self-assembled ZnWO anion was selectively immobilized into LDH in the presence of undesired anions, and (b) the structure of ZnWO was retained after the anion-exchange process.

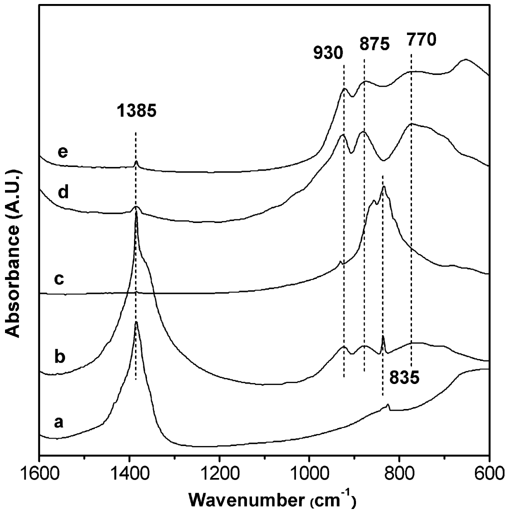


**Fig. 1.** FT-IR spectra of (a) LDH-$NO_3$ support, (b) dried sample from self-assembled ZnWO solution, (c) pure $Na_2WO_4$, (d) purified Na-ZnWO salt, and (e) LDH-ZnWO.

The powder XRD patterns show that the basal spacing of LDH increased from 0.82 nm for the LDH-$NO_3$ support to 1.49 nm for the LDH-ZnWO, indicating a LDH-ZnWO gallery height of 1.02 nm (see Fig. S1 in Supporting information). This gallery height is in agreement with the diameter of the short axis of sandwich-type ZnWO anion (dimensions of ∼1.0 to ∼1.5 nm) [6,18]. The absence of the reflections of LDH-$NO_3$ and Na-ZnWO in the XRD pattern of LDH-ZnWO indicates that the mixture of LDH-$NO_3$ and Na-ZnWO did not exist in the LDH-ZnWO sample. These results demonstrate that the ZnWO anion was successfully incorporated into the interlayer of LDH by the anion-exchange process [19] and had a uniform dispersion in the LDH host. An additional XRD peak with *d*-spacing of ∼1.2 nm also appeared, which can be ascribed to the ZnWO immobilized on the external surface of the LDH layers [20].

The TEM images of the LDH-ZnWO are given in Fig. 2. The bright-field TEM image shows well-developed hexagonal plates for LDH host, and the dark-field TEM image exhibits a uniform dispersion of ZnWO nanoclusters (shown as small white dots) throughout the LDH, is in agreement with the XRD findings. ICP-AES of LDH-ZnWO revealed a W content of 41.9% and a Zn content of 3.8 wt%. The W:Zn molar ratio of 3.9 is consistent with the theoretical value of 3.8 for ZnWO. According to the ICP-AES and TGA results, the chemical formula of LDH-ZnWO was estimated to be $Mg_{0.73}Al_{0.27}(OH)_2(ZnWO)_{0.023}\cdot 1.1H_2O$, with a ZnWO loading of ca. 0.12 $mmol\,g^{-1}$.

The foregoing characterization results suggest that the LDH support enables the direct immobilization of self-assembled ZnWO anion in the presence of undesired anions. The success of this selective anion-exchange process may be attributed to two factors: (a) The ZnWO anion has higher negative charge than other anions, and (b) the LDH layer has high positive charge density and thus a stronger interaction with the ZnWO anion. We applied a hydrothermal treatment to verify the LDH-ZnWO's structural stability. After the LDH-ZnWO was treated with water in an autoclave at 120 °C for 7 days, FTIR and ICP-AES detected no apparent changes in structure or components. This finding confirms the LDH-ZnWO's good hydrothermal stability.

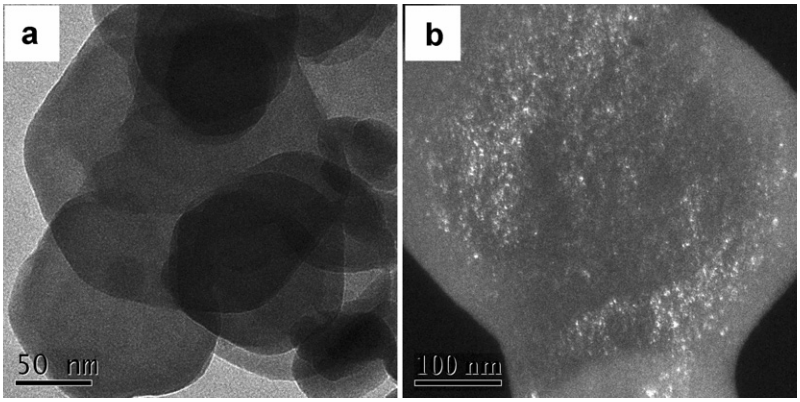
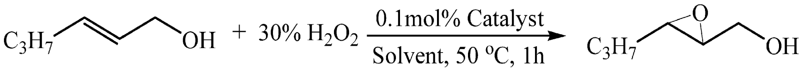


**Fig. 2.** TEM images of LDH-ZnWO: (a) bright field image, (b) dark field image, exposing ZnWO nanoclusters.

**Table 1**
Epoxidation of (*E*)-2-hexen-1-ol with aqueous $H_2O_2$ catalyzed by LDH-ZnWO[a]



| Entry | Catalyst | Solvent | Yield (%)[b] | Selectivity (%)[b] |
|---|---|---|---|---|
| 1 | LDH-ZnWO | Hexane | 39 | 98 |
| 2 | LDH-ZnWO | THF | 53 | 97 |
| 3 | LDH-ZnWO | $H_2O$ | 58 | 99 |
| 4 | LDH-ZnWO | Dioxane | 72 | 98 |
| 5 | LDH-ZnWO | $CH_3CN$ | 80 | 99 |
| 6 | Reuse 1[c] | $CH_3CN$ | 87 | 99 |
| 7 | Reuse 2[c] | $CH_3CN$ | 93 | 99 |
| 8 | Reuse 3[c] | $CH_3CN$ | 95 | 99 |
| 9 | Reuse 6[c] | $CH_3CN$ | 92 | 99 |
| 10 | Na-ZnWO[d] | $CH_3CN$ | 93 | 95 |

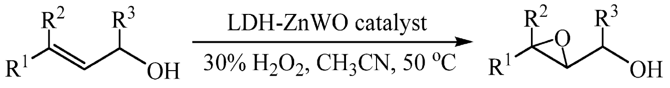
[a] Reaction conditions: 1 mmol (*E*)-2-hexen-1-ol, 2 mmol of aqueous $H_2O_2$, 0.1 mol% of LDH-ZnWO, 0.2 mmol *n*-dodecane, 0.2 mL of solvent, 50 °C, 1 h.
[b] Determined by GC with an internal standard technique.
[c] Recycling experiment.
[d] Homogeneous epoxidation.

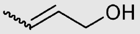
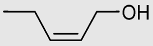
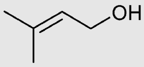
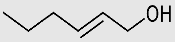
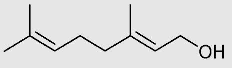
We investigated the activity of the LDH-ZnWO catalyst for the epoxidation of (*E*)-2-hexen-1-ol with aqueous $H_2O_2$ at 50 °C. We evaluated various solvents to identify the appropriate conditions for the reaction with 0.1 mol% of LDH-ZnWO (Table 1, entries 1–5). The yield of this heterogeneous catalytic reaction proved to be solvent-dependent, with $CH_3CN$ giving the better results (80% yield and 99% selectivity after 1 h). In addition, the LDH-$NO_3$ support alone demonstrated negligible activity ($<2\%$ conversion after 1 h with $CH_3CN$ solvent).

We also evaluated the reusability of the LDH-ZnWO catalyst, which was successfully recycled seven times in the epoxidation of (*E*)-2-hexen-1-ol with no apparent loss of activity or selectivity (Table 1, entries 5–9). Significantly, the LDH-ZnWO catalyst exhibited comparable reactivity to and slightly higher selectivity than the homogeneous Na-ZnWO catalyst (entry 10) under identical conditions. LDH-ZnWO's higher selectivity may be due to the benefits of the basic LDH host, which may suppress the acid-catalyzed epoxide hydrolysis [17]. The LDH-ZnWO catalyst could be readily separated from the reaction mixture by filtration. The FTIR spectrum of the recovered LDH-ZnWO catalyst comfirmed retention of the original ZnWO structure, and ICP-AES analysis of the filtrate indicated no leaching of W and Zn species during epoxidation. After the catalyst was removed at about 50% conversion of the (*E*)-2-hexen-1-ol, no further epoxidation was detected in the filtrate after 3 h with additional aqueous $H_2O_2$. These results further demonstrate the strong interaction between the ZnWO and the LDH host and show that LDH-ZnWO acts as a real heterogeneous catalyst in aqueous epoxidation reactions. Interestingly, an increase in catalytic activity was seen in the first three recyclings of the LDH-ZnWO catalyst; this enhanced activity may be due to the increased number of active sites available in the recycled catalyst.

To extend the scope of the substrates for this heterogeneous catalytic epoxidation, we carried out the epoxidation of various allylic alcohols with aqueous $H_2O_2$ under the optimal conditions. As shown in Table 2, all allylic alcohols were converted to the corresponding epoxides with high yields and selectivities (up to 99%). The LDH-ZnWO catalyst demonstrated high turnover frequencies (TOF $>$ 1000 $h^{-1}$) for the epoxidation of various allylic alcohols; in particular, for geraniol (entry 6), the regioselective epoxidation proceeded smoothly to produce 2,3-epoxy alcohol with a TOF of 1720 $h^{-1}$. Significantly, excellent catalytic activity (entries 3 and 4) was achieved even at a very low catalyst loading of only 0.01 mol%, unequivocally demonstrating the high efficiency (TOF up to 18,000 $h^{-1}$ for entry 3) of the LDH-ZnWO catalyst. To the best of our knowledge, compared with the typically reported productivities of heterogenized POM catalysts (TOF = 1–500 $h^{-1}$) [2,6–8,21], these are among the highest values reported for the selective epoxidation of allylic alcohols. It is noteworthy that the excellent activity and recyclability of this type of catalyst can meet the requirements for continuous operation with a fixed-bed reactor.

**Table 2**
Heterogeneous epoxidation of various allylic alcohols with aqueous $H_2O_2$ catalyzed by LDH-ZnWO catalyst[a]



| Entry | Substrate | Time (h) | Yield (%)[b] | Selectivity (%)[b] | TOF ($h^{-1}$)[c] |
|---|---|---|---|---|---|
| 1 |  | 0.5 | 96 | 98 | 1920 |
| 2 |  | 1 | 93 | 99 | 1160 |
| 3[d] |  | 0.5 | 90 | 99 | 18,000 |
| 4[d] |  | 6 | 89 | 99 | 2300 |
| 5 |  | 1.5 | 90 | 99 | 1030 |
| 6 |  | 0.5 | 86 | 98 | 1720 |

[a] Reaction conditions: 1 mmol substrate, 2 mmol of aqueous 30% $H_2O_2$, 0.1 mol% of LDH-ZnWO, 0.2 mmol *n*-dodecane, 0.2 mL of $CH_3CN$, 50 °C.
[b] Determined by GC or GC–MS with an internal standard technique.
[c] Based on the epoxide yield after 0.5 h, and given in mmol epoxide produced per mmol of ZnWO in the catalyst per hour.
[d] 10 mmol substrate, 20 mmol of aqueous 30% $H_2O_2$, 0.01 mol% of LDH-ZnWO, 1 mL of $CH_3CN$, 50 °C.

## 4. Conclusion

Here we have reported the first example of direct immobilization of a self-assembled POM catalyst in LDH for use as a robust heterogeneous epoxidation catalyst. The catalyst is readily prepared through a concise route using inexpensive starting materials and exhibits high dispersion and good hydrothermal stability. The heterogeneous epoxidation of a range of allylic alcohols proceeds in high yields. Of significant practical importance are the findings of excellent activity (TOF up to 18,000 $h^{-1}$) and the ability to readily recover and reuse the catalyst with no apparent loss of activity.

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## Supporting information

The online version of this article contains additional supporting information.

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