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Modular polyoxometalate-layered double hydroxides as efficient heterogeneous sulfoxidation and epoxidation catalysts

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Abstract: Selective sulfoxidation of sulfides and epoxidation of olefins are two types of important organic reactions and the corresponding products of sulfoxides, sulfones and epoxides are widely used as raw materials in industrial processes. The fabrication of one efficient catalyst for both reactions, remains a challenging task. In this paper, we report the preparation of a highly efficient heterogeneous catalyst of Mg₃Al-ILs-La(PW₁₁)₂ usina an exfoliation/assembly approach. The catalyst was characterized by FT-IR, XRD, TG/DTA, BET, XPS, ²⁹Si CP/MAS NMR, the ²⁷AI-MAS NMR, SEM, HRTEM, EDX etc. The designed catalyst showed high efficiency and selectivity for sulfoxidation of sulphides and epoxidation of olefins under mild conditions at a production rate of 208 mmol g⁻¹ h⁻¹ and 31 mmol g⁻¹ h⁻¹, respectively. Moreover, the Mg₃Al-ILs-La(PW₁₁)₂ can be recycled and reused at least 5 times without obvious decrease of its catalytic activity. The scaled-up experiments revealed that the catalyst retained its efficiency and robustness, demonstrating the catalyts' great potential for industrial applications.

Introduction

Polyoxometalates (POMs) are a class of molecular metal oxide anions, often incorporating V, Mo, W, or Nb etc., in their highest oxidation states.^[1-4] The remarkable properties of POMs such as redox potential, electron-transfer properties, thermal and oxidative stability, acidity, etc., can be finely tuned by incorporation of appropriate addenda metal ions and/or counterions, which endow superior catalytic performance in numerous industrial processes.^[5-8] However, the industrial application of POM-based homogeneous catalytic systems has been restricted mainly due to poor separation ability, decomposition issues, environmental concerns, and its high operational cost. Consequently, design of POM-based advanced heterogeneous catalysts has long been and will continue to be the focus for a potentially alternative way to overcome the above limitations and to tune the POM-based material's functionality.

The solidification and immobilization are the two main

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.xxxxxxxxx techniques that have been widely adopted for POM-based heterogeneous catalysts^[9-10] such as the incorporation of POMs into porous inorganic supports (silica,^[11-12] zeolite,^[13] Al₂O₃^[14] etc.). However, the immobilization on the aforementioned inorganic supports is usually accompanied by a series of issues which compromise the performance of the designed catalytic systems such as hydrolytic and thermal stability under oxidative conditions; poor mass transfer and accessibility of the active centres; catalyst leaching issues.^[10,15] These inherent limitations prevent the development of efficient catalytic systems with desirable functionality and specifications. Thus, it is of fundamental importance to explore appropriate preparation methodologies that will allow the design of efficient, recyclable, stable, and environmentally benign heterogeneous catalytic systems for various industrial applications.

Layered double hydroxides (LDHs) or hydrotalcite-like compounds are a large family of two-dimensional (2D) anionic clays with the general formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}[Ax/n]n- M_2O$, where M²⁺ and M³⁺ are di- and trivalent metal cations and [A] are inorganic or organic charge-compensating anions located in the interlayer galleries.^[16-17] Each hydroxyl group in the LDH layers is oriented towards the interlayer region forming a network of hydrogen bonds to the interlayer anions and water molecules.^[18] LDHs provide a flexible and modular confined space which can be modified by varying the size and the structure of guest molecules. Intercalation of catalytically active species into the interlayer galleries to generate host-guest supramolecular intercalation structures with desirable physical and chemical properties has been proven to be an elegant approach for improving the stability and recyclability of the catalytic system. However, the poor mass transfer of the organic substrates within the interlayer galleries and effective interaction with the active centres of the intercalated catalysts is a major challenge that needs to be taken into careful consideration.

lonic liquids (ILs) have been extensively investigated as novel green solvents or alternative catalytic materials, which are currently receiving keen interest owing to their unique properties, such as negligible volatility and remarkable solubility.^[19-21]

Based on the above considerations, we demonstrate a successful preparation of a novel heterogeneous catalyst of Mg₃Al-ILs-La(PW₁₁)₂ by intercalation the designed catalytically active POMs into the ILs covalently modified LDHs. Catalytic tests indicate that the designed catalyst Mg₃Al-ILs-La(PW₁₁)₂ exhibits excellent activity for selective sulfoxidation of sulfides and epoxidation of olefins under mild conditions, coupled with easy recovery and steady reuse.

Structural characterization

As shown in Fig. 1a, FT-IR spectrum of La(PW₁₁)₂ exhibits characteristic peaks centred at 1093, 950, 882 and 769 cm⁻ ¹, which can be attributed to the asymmetric and symmetric vibrations of W-Ot, asymmetric vibration of W-Oc-W and asymmetric vibration of W-Oe-W (t, terminal; c, cornersharing; e, edge-sharing),[22] respectively. These W-O stretching bands can be clearly observed in the corresponding FT-IR spectra of Mg₃Al-ILs-La(PW₁₁)₂ and Mg₃Al-La(PW₁₁)₂. Taking Mg₃Al-ILs-La(PW₁₁)₂ as an example, the W-O stretching vibrations gave peaks located at 1089, 954, 889 and 775 cm⁻¹, respectively, which are slightly shifted due to the strong electrostatic interactions and hydrogen bonding between the host layers and intercalated POMs.^[23] Moreover, the peak at 1051 cm⁻¹ can be assigned to the stretching vibration of the P-O bond, which appears at 1046 cm⁻¹ in the spectrum of $La(PW_{11})_2$. The FT-IR spectrum of Mg₃Al-ILs-La(PW₁₁)₂ also exhibits new C-H stretching vibrations at 2930 and 2856 cm⁻¹ due to the alkyl chain -CH₂ and -CH₃ groups, while the C=N stretching appears at 1658 cm-1 originating from the imidazole ring of ILs, respectively. Additionally, the peak located at 448 cm⁻¹ is assigned to the O-M-O (M = Mg or Al) vibration of the brucite-like layers of the LDHs.[24]



Figure 1. a) FT-IR spectra of (i) La(PW₁₁)₂, (ii) Mg₃Al-ILs-La(PW₁₁)₂, (iii) Mg₃Al-La(PW₁₁)₂, (iv) Mg₃Al-NO₃; b) The ²⁹Si CP/MAS NMR spectrum of Mg₃Al-ILs-La(PW₁₁)₂ and inset picture shows the structure model of T³; c) XRD patterns of (i) Mg₃Al-NO₃; (ii) Mg₃Al-La(PW₁₁)₂, (iii) Mg₃Al-ILs-La(PW₁₁)₂; d) TG-DTA profiles of (i) Mg₃Al-ILs-La(PW₁₁)₂ and (ii) Mg₃Al-La(PW₁₁)₂.

It should be noted that the stretching band at 1384 cm⁻¹ for Mg₃Al-NO₃ due to the N-O vibration^[25] of NO₃⁻ appears to be weak in the corresponding FT-IR spectra of Mg₃Al-ILs-La(PW₁₁)₂ and Mg₃Al-La(PW₁₁)₂, indicating almost quantitative exchange of NO₃⁻ by POM clusters. The above observations demonstrate that the ILs are grafted onto the layers of LDHs and the La(PW₁₁)₂ clusters are intercalated into LDHs successfully. The

FT-IR spectra of PW₁₂, P₂W₁₈, Mg₃Al-ILs-PW₁₂, Mg₃Al-ILs-P₂W₁₈ are shown in Fig. S1.

Additional confirmation of the catalysts' composition and structural features was provided by the (CP/MAS) NMR studies. As shown in Fig. 1b, the solid-state ²⁹Si cross-polarization magic-angle spinning (CP/MAS) NMR spectrum of Mg₃Al-ILs-La(PW₁₁)₂ exhibits a resonance peak centred at -66.4 ppm, which corresponds to T³ [Si(OM)₃].^[26] The presence of T³ signal indicates there are M-O-Si bonds around Si atom (M = Mg or Al). These results confirm that the ILs are tethered onto the layers of LDHs covalently, resulting in the formation of Mg-O-Si and/or Al-O-Si within the interlayer space.

As shown in Fig. 1c, the XRD pattern of Mg₃Al-NO₃ exhibit a reflection peak centered at $2\theta = 9.88$, which is attributed to the characteristic reflection of basal plane (003) and corresponds to a spacing value of $d_{003} = 0.89$ nm. After the intercalation of the La(PW₁₁)₂ anions, a shift of the (003) reflection to lower angles was observed ($2\theta = 6.28$). This change corresponds to a basal spacing value of d_{003} =1.42 nm, indicating an increase of the interlayer region due to the intercalation of the La(PW₁₁)₂ species in Mg₃Al-ILs-La(PW₁₁)₂. The height of the interlayer region value of 0.94 nm was calculated by subtracting the dimensions of the host layer (0.48 nm) from the value of the d_{003} spacing (1.42 nm) of the Mg₃Al-ILs-La(PW₁₁)₂ composite. The obtained value is in good agreement with the width of the POM cluster (with dimensions of just below 1 nm). This indicates that the La(PW₁₁)₂ anion's "long axis" is oriented parallel in the interlayer region of the LDHs .

The TG-DTA of Mg₃Al-La(PW₁₁)₂ (Fig. 1d) exhibits threestage weight losses, where the first one takes place within the range of 25 to 250 °C and is attributed to the loss of water molecules adsorbed on the surface and interlayer region; the second weight loss can be attributed to the collapse of the layered structure of LDHs and the third weight loss corresponds to the decomposition of La(PW₁₁)₂. In the case of Mg₃Al-ILs-La(PW₁₁)₂, three main weight-loss stages can be observed, in which the first weight loss of 6.46 % between 25 and 240 °C can be ascribed to the removal of water molecules; the second weight loss of 13.10 % takes place between 240 and 650 °C which corresponds to the collapse of the layered structure and decomposition of the ionic liquid and the third weight loss of 1.87 % between 650 and 900 °C is due to the decomposition of La(PW₁₁)₂.

As shown in Fig. 2a, the photoelectron peaks of Mg, Al, C, O, N, P, La and W can be clearly identified from X-ray photoelectron spectroscopy (XPS). The XPS spectrum of W(4f) photoemission (Fig. 2b) consists of two peaks originating from the spin orbital splitting of the W4f_{7/2} and W4f_{5/2} at 35.1 eV and 37.1 eV, respectively, which can be ascribed to the W in the W-O bond configuration and typically observed for W⁶⁺.^[28] As shown in Fig. 2c, Mg₃Al-ILs-La(PW₁₁)₂ exhibits typical type-IV adsorption isotherms, and H3 type hysteresis loops at higher relative pressure (*P/Po*>0.5), indicating the presence of both interlayer and interparticle mesopores structure. The pore size distribution calculated by the Barrett-Joyner-Halenda (BJH) method shows a peak centred at around 3.8 nm (Inset Fig. 2c). The Mg₃Al-ILs-La(PW₁₁)₂ exhibits a Brunauer-Emmett-Teller

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(BET) surface area of 43.99 m²/g with a total pore volume of 0.18 cm³/g. The N₂ adsorption-desorption isotherm and the pore size distribution of Mg₃Al-La(PW₁₁)₂ are shown in Fig. S5 while a comparison of their physicochemical properties is shown in Table S1.



Figure 2. a) XPS survey spectrum of Mg₃Al-ILs-La(PW₁₁)₂; b) XPS spectrum for the W_{4f} core level of Mg₃Al-ILs-La(PW₁₁)₂; c) The N₂ adsorption-desorption isotherm and the pore size distribution (inset picture) of Mg₃Al-ILs-La(PW₁₁)₂; d) The ²⁷Al-MAS-NMR spectra of (i) Mg₃Al-NO₃, (ii) Mg₃Al-La(PW₁₁)₂, and (iii) Mg₃Al-ILs-La(PW₁₁)₂.

The ²⁷Al resonance line positions are very sensitive to the coordination number and are expected to appear within the range of -5 to 15 ppm for the octahedral geometry of AIO₆ sites. ^[26] As shown in Fig. 2d, the solid state ²⁷AI-MAS-NMR spectrum of Mg₃Al-NO₃ exhibits a strong single signal at ~10.9 ppm, indicating the presence of octahedral geometry of AIO₆ sites in the brucite-like layers.^[29-31] In the case of $Mg_3AI-La(PW_{11})_2$ and Mg₃Al-ILs-La(PW₁₁)₂, the ²⁷Al-MAS-NMR signals are located almost at the same position (with a slight shift to low field chemical shift) in comparison to the Mg₃Al-NO₃. This observation indicates that the brucite-like layered structure retains its integrity upon intercalation of the POMs. Based on the TG-DTA, ICP and elemental analysis considerations, the formula of the composite material of Mg₃Al-ILs-La(PW₁₁)₂ was identified as Mg_{0.75}Al_{0.25}(OH)_{1.87}[O₃SiC₁₄H₂₈N₂]_{0.042}[PF₆]_{0.036} [La(PW₁₁O₃₉)₂] 0.0225 · 0.72H₂O (the POM loading, La(PW₁₁)₂, found to be 104.56 µmol/g, W=42.3 wt. %, ILs= 5.9 wt.%).

Scanning Electron Microscopy studies of the composite material was used in order to obtain further information regarding the morphology of the catalyst in solid state. The SEM images of the as-prepared Mg₃Al-ILs-La(PW₁₁)₂ (Fig. 3) showed uniform porous stacking of sheet-like crystallites with an average size of ~1 μ m (Fig. 3a-c). The porous sheet-like morphology may be due to the high percentage of active coordinatively unsaturated atoms located at the edges on the crystallites.^[32] Energy-dispersive spectroscopy (EDX) mapping (Fig. 3d) revealed the uniform dispersion of the composition element Mg, Al, C, O, W, which is closely related to the unique structural

architecture of LDHs. In LDHs, the divalent (Mg²⁺) and trivalent (Al³⁺) cations can be highly dispersed within the brucite-like layers.^[33] Moreover, the POMs are dispersed and orderly arranged in the two-dimensional (2D) confined gallery space. HRTEM images (Fig. 3e-g) and EDX results revealed the presence of highly dispersed black spots of 1.5 ~ 2 nm in diameter, which are in good agreement with the size of La(PW₁₁₎₂ clusters.



Figure 3. SEM images of a-c) Mg₃Al-ILs-La(PW₁₁)₂, inset picture in image b shows the water contact angle measurements of Mg₃Al-ILs-La(PW₁₁)₂, d) compositional EDX mapping of the Mg₃Al-ILs-La(PW₁₁)₂; HRTEM images of e-f) Mg₃Al-ILs-La(PW₁₁)₂ and g) its corresponding EDX.

In order to gain better understanding of the interactions between the catalyst and substrates under the employed experimental conditions, the amphiphilic property of the intercalated catalyst was investigated (inset picture in Fig. 3b). The LDH layers are hydrophilic due to the presence of numerous hydroxyl groups and water molecules in the interlayer galleries. However, when a water droplet contacts the sheet of Mg₃Al-ILs-La(PW₁₁)₂, it forms a contact angle of 136°, indicating a moderate hydrophobicity and excellent surface wettability for the organic substrate. This observation suggests that the hydrophobicity of the intercalated catalyst is increased due to the modification of the LDHs layers with ionic liquids, leading finally to easier access and more effective interaction of the substrate with the catalytic site. Additional, SEM, HRTEM, EDX spectra of the Mg₃Al-ILs-PW₁₂ and Mg₃Al-ILs-P₂W₁₈ composites are reported in the ESI (Fig. S6).

Selective sulfoxidation of thioanisole



Scheme 1. Model reaction of selective oxidation of thioanisole.

Oxidative transformations of organic compounds under mild conditions are of great importance in industrial processes and synthetic organic chemistry.^[34-35] The selective oxidation of sulfides to sulfoxides and sulfones is a pivotal reaction due to its use in chemical industry, medicinal chemistry and biology.^[14] In this work, we aim at exploring the efficiency of different catalysts for selective oxidative of thioanisole in the presence of different substrates and H_2O_2 (Scheme 1). In order to evaluate the feasibility, we used thioanisole as a model substrate in the presence of H_2O_2 (30 %) as the oxidant for the model reaction.

Table 1. Selective oxidation of thioanisole in methanol with H₂O₂ by different

catalysts.	[a]		
Entry	Catalyst	Conv ^[b] (%)	Selec ^[b] (%)
1	$Mg_3AI-La(PW_{11})_2$	80.5	91.3
2	Mg ₃ Al-ILs-La(PW ₁₁) ₂	99.9	97.6
3	Mg ₃ Al-NO ₃	25.4	98.6
4	ILs	73.6	98.2
5	Mg ₃ Al-NO ₃ +ILs+ La(PW ₁₁) ₂	79.4	95.8
6	Mg(OH) ₂	18.6	82.5
7	AI(OH) ₃	17.8	83.4
8	None	17.3	82.5
9	Mg ₃ Al-ILs-PW ₁₂	83.8	88.7
10	Mg ₃ Al- ILs-P ₂ W ₁₈	81.7	91.7

[a] Reaction conditions: 1 mmol of thioanisole, 1 mmol of H₂O₂ (30 wt.%), 20 mg catalyst, T = 25 °C, t = 1 h. [b] Conversion and selectivity were determined by GC analysis using reference standards. Assignment of product was analysed by ¹H NMR and ¹³C NMR in Fig. S7.

As shown in Table 1, the Mg₃Al-La(PW₁₁)₂ shows 80.5 % conversion and 91.3 % selectivity (entry 1). Notably, the Mg₃Al-ILs-La(PW₁₁)₂ exhibits excellent catalytic performance with 99.9 % conversion and 97.6 % selectivity (entry 2) under the same experimental conditions. However, only 17.3 % conversion of sulfoxidation is obtained in the absence of catalyst (entry 8). Moreover, the reaction proceeds sluggishly when physical mixture of the individual components of the composite material, or the parent LDH (Mg₃Al-NO₃), and/or ILs (entries 3-5) was used as catalysts. To prove that the catalytic activity is not the effect of potential impurities, we studied the efficiency of Mg(OH)₂ and Al(OH)₃ (entries 6 and 7) which revealed only 18.6 and 17.8 % conversion, respectively. The control experiments (entries 9-10) exhibits inferior catalytic activity in the case where other classical POMs such as Keggin (Mg₃Al-ILs-PW₁₂) and Well-Dawson (Mg₃Al-ILs-P₂W₁₈) were incorporated in the LDH. The results suggest that the Mg₃Al-ILs-La(PW₁₁)₂ is one of the most efficient catalysts for sulfoxidation reactions.

The oxidation of organosulfur compounds involves an electrophilic attack of an activated peroxo species to the sulfide. ^[36] The catalytic activity for such sulfoxidation is supposed to

increase as a function of the electron deficiency on the catalytic active center.^[15] Our previous work have demonstrated that grafting of ionic liquids onto LDHs nanosheets enhances the mass transfer in solid-liquid interface by improving the accessibility of the substrates to the active species.^[21] Therefore, the above experimental results account for the observed difference of the catalytic activity when we use different catalysts. In addition, these results strongly support the importance of the synergistic effect between the components of the heterogeneous catalyst Mg_3AI -ILs-La(PW_{11})₂, which is reflected in the enhancement of the overall catalytic performance.



Figure 4. Effect of solvents on sulfoxidation of thioanisole by Mg₃Al-ILs-La(PW₁₁)₂. Reaction conditions: 1 mmol of substrate, 1 mmol of H₂O₂ (30 wt. %), 20 mg catalyst, 200 μ L of solvent, 25 °C, 1 h.

A series of solvents have been tried to investigate their effect on the catalytic activity, and the results showed a conversion of 99.9%, 93.7%, 91.6%, 87.1%, 83.8%, 90.6%, 87.3%, 79.5%, 77.4%, 82.3% for methanol, ethanol, *i*-propanol, 1-butanol, acetonitrile, acetone, water, dichloromethane, trichloromethane and solvent-free conditions, respectively (Fig. 4). The observed difference can be attributed to solvation effects and different interactions between thioanisole and the solvents. As a result, the optimized solvent for such a sulfoxidation reaction is methanol.

Kinetic study of sulfoxidation of thioanisole

In an effort to obtain the kinetic parameters for the model reaction, parallel experiments have been carried out under the optimized conditions. Taking the Mg₃Al-ILs-La(PW₁₁)₂ as an example, the reaction proceeds smoothly at room temperature. Conversion and $\ln(C_t/C_0)$ are plotted against reaction time in Fig. 5, where C_0 and C_t are the initial thioanisole concentration and the concentration of thioanisole at time t, respectively. The Mg₃Al-ILs-La(PW₁₁)₂ exhibits excellent catalytic activity and the conversion can reach 99 % with above 97 % selectivity of the corresponding sulfoxide in 1 h. The linear fit of the data reveals that the catalytic reaction follows pseudo-first-order kinetics for selective oxidation of thioanisole reaction ($R^2 = 0.992$). The observed rate constant k for the selective oxidation reaction was determined to be 0.069 min⁻¹ on the basis of Eqs. (1) and (2). Thus, the catalyst exhibits high catalytic efficiency for the sulfoxidation reaction, and the catalytic reaction obeys pseudofirst-order kinetics with > 97 % selectivity of the corresponding

sulfoxide at a production rate of 208 mmol g⁻¹ h⁻¹ (mmol product produced per gram of catalyst per hour).



Figure 5. Kinetic profiles of oxidation of thioanisole under the optimized conditions; Reaction conditions: 1 mmol of thioanisole, 1 mmol of H₂O₂ (30 wt.%), 20 mg catalyst, 200 μ L methanol, T = 25 °C.

In order to evaluate the applicability of the heterogeneous catalyst Mg_3AI -ILs-La(PW₁₁)₂, a number of thioether-based compounds were used as substrates under the optimized reaction conditions (Table 2). The results demonstrate that we can achieve excellent conversion and selectivity for most thioethers (entries 1-9, 11). However, the benzyl phenyl sulfide showed relatively low conversion and poor selectivity, which might be attributed to the increased steric hindrance (entry 10). When the substrate/H₂O₂ molar ratio is 1:2, all the substrates can be selectively oxidized to the corresponding sulfone with excellent selectivity (Table S2).

Efficiency for selective oxidation of thioanisole to sulfoxides

The catalytic selective oxidation of sulfides using various catalysts that have been reported in the literature is summarized in Table 3. For example, Wang *et al.* reported a novel ionic liquid-based polyoxometalate (POM) catalytic system that shows

exclusive oxidation of sulfoxide at room temperature at a very short time.^[37] However, it should be noted that some of these reported catalytic systems suffer from low activity, hydrolytic and thermal stability under oxidative conditions, catalyst leaching, recycling issues, *etc*.

Table 2. Selective	oxidation	of	various	sulfides	to	sulfoxides	catalyzed	by
Mg ₃ Al-ILs-La(PW ₁₁)	2 in metha	nol.	[a]					



[a] Reaction conditions: 1 mmol substrate, 1 mmol of H_2O_2 (30 wt.%), 20 mg catalyst, T = 25 °C. [b] Conversion and selectivity were determined by GC analysis using reference standards.

Another important factor is the high cost of some catalytic systems which renders them unsuitable candidates for large scale experiments or industrial applications. In contrast, the sulfoxidation of thioanisole using Mg₃Al-ILs-La(PW₁₁)₂ exhibits high efficiency and selectivity, along with excellent stability, recyclability and very efficient use of H₂O₂ (Substrate:H₂O₂ = 1:1) during the catalytic cycles (Table 2 and Table 3, entry 13), which renders it an ideal candidate for large scale experiments.

Entry	Catalyst	H ₂ O ₂ (equiv.)	T.(°C)	Time (h)	Conv. (%)	Sel.of sulfoxide	Ref		
1	WO ₃ /MCM-48	1.1	rt	4	95	97	38		
2	TiO ₂	1.2	80	3	100	0.5	39		
3	(TBA) ₂ [SeO ₄ {WO(O ₂) ₂ } ₂]	1	20	2	99	90	40		
4	(TBA) ₄ [γ-SiW ₁₀ O ₃₄ (H ₂ O) ₂]	0.2	32	1	98	99	41		
5	Fe ₃ O ₄ @SiO ₂ APTES	3	rt	1.5	96	95	42		
6	WO ₄ ²⁻ /silica-NH ₃ ⁺	3	rt	1.5	82	100	43		
7	BisILs-C ₈ H ₁₇ -[W ₂ O ₃ (O ₂) ₄]	1.1	rt	1.5	98.6	-	44		
8	DA-La(PW ₁₁) ₂	1	25	6	91	99	45		

Table 3. Oxidation of thioanisole to sulfoxides by different catalysts with H_2O_2 as oxidant.

9	[C4mim]₂HPM	1.1	25	0.5	98.8	98.4	37
10	[PO4[WO(O2)2]4]@PIILP	2.5	rt	0.25	95	96	46
11	Ti-IEZ-MWW	1	rt	2	99	94	47
12	Mg ₃ Al-P ₂ W ₁₇ Zn	1	rt	6	96	100	15
13	Mg ₃ AI-ILs-La(PW ₁₁) ₂	1	25	1	99	98	This work

Epoxidation of olefin

The efficiency of the Mg₃Al-ILs-La(PW₁₁)₂ composite was further evaluated in olefin epoxidation reactions (Fig. 6). In an effort to identify the optimized epoxidation reaction conditions, a series of solvents, concentration and the substrate/H₂O₂ molar ratios were carefully explored (Fig. S 9-10). The optimum conditions are: *cis*-cyclooctene 1 mmol, H₂O₂ 3 mmol, 1 ml CH₃CN, 40 mg catalyst. We investigated the effect of reaction time on the epoxidation of *cis*-cyclooctene by Mg₃Al-ILs-La(PW₁₁)₂. The reaction conversion increases as a function of the reaction time. However, when the reaction temperature reaches to 70 °C, the reaction conversion does not increase anymore. Thus, the experiments to determine the kinetic parameters for the epoxidation of *cis*-cyclooctene were carried out at 70 °C.



Figure 6. Top: schematic diagram of the catalytic epoxidation of *cis*-cyclooctene. a) Effect of reaction time on epoxidation of *cis*-cyclooctene by Mg₃Al-ILs-La(PW₁₁)₂ under different temperatures b) Kinetic profiles of the epoxidation reaction. Reaction conditions: 1 mmol of substrate, 3 mmol H₂O₂ (30 wt. %), 40 mg catalyst, 1 ml CH₃CN; T = 70 °C.

Conversion and $\ln(C_t/C_0)$ are plotted against reaction time in Fig. 6b, where C_0 and C_t are the initial *cis*-cyclooctene concentration and *cis*-cyclooctene concentration at time t, respectively. The linear fit of the data reveals that the catalytic reaction shows pseudo-first-order kinetics for the epoxidation reaction ($R^2 = 0.984$). The observed rate constant *k* was determined to be 0.7647 h⁻¹ on the basis of Eqs. (1) and (2). The Mg₃Al-ILs-La(PW₁₁)₂ shows pretty good catalytic activity producing 31 mmol g⁻¹ h⁻¹ (mmol product produced per gram of catalyst per hour) of oxidation product while the conversion and selectivity reached a value of 99 % in 5 h.

The Mg₃Al-ILs-La(PW₁₁)₂ exhibited high conversion and selectivity (Table 4) in the epoxidation of other well-known olefins such as cyclohexene and cyclododecene (entries 2-3).

Moreover, the catalyst can be applied to the epoxidation of allylic alcohols (*trans*-2-hexene-1-ol) with 93 % conversion and 95 % selectivity (entry 4). The catalytic efficiency of previously reported systems for the epoxidation of olefin substrates are summarized in Table S3 (see the Supporting Information). The results confirm that the Mg₃Al-ILs-La(PW₁₁)₂ is an excellent heterogeneous catalyst for the epoxidation of olefins.

Table	4.	The	epoxidation	of	various	substrates	over	catalyst	Mg₃AI-ILs-
La(PW	11)2.	[a]							

Entry	Substrates	Time (h)	Conv ^[b] (%)	Selec ^[b] (%)
1	cis-cyclooctene	5	97	99
2	cyclohexene	5	96	99
3	cyclododecene	12	82	99
4	trans-2-hexene-1-ol	2	93	95

[a]Epoxidation of different substrates with H_2O_2 catalyzed with $Mg_3AI-ILs-La(PW_{11})_2$. Reaction conditions: 1 mmol of substrate, 40 mg catalyst, 3 mmol H_2O_2 (30 wt.%), 1 ml CH₃CN; T = 70 °C. [b] Conversion and selectivity were determined by GC analysis using reference standards.



Figure 7. a) Catalytic reusability of Mg₃Al-ILs-La(PW₁₁)₂ for sulfoxidation of thioanisole; b) Experiment to prove the nature of heterogeneous catalyst; c) FT-IR spectra and d) solid-state ²⁹Si CP/MAS NMR spectra of the fresh and used Mg₃Al-ILs-La(PW₁₁)₂.

The catalyst's stability and recyclability are essential requirements for larger scale applications.^[48-49] In order to evaluate the recyclability of the catalytic system, we repeated the selective oxidation of thioanisole using Mg₃Al-ILs-La(PW₁₁)₂. The catalyst was separated from the reaction mixture by centrifugation, washed with acetone, dried and re-used by addition of fresh substrate and H₂O₂ (30 wt. %) at 25 °C (Fig. 7a).

During the five-run recycling test, the conversion found to be 99.9 %, 98.2 %, 98.4 %, 97.8 %, 97.5 %, 97.1 %, while the selectivity remains above 98 %. Inductively coupled plasma atomic emission analysis (ICP-AES) of the recycled catalyst confirms that the polyoxometalate is stable by intercalating into the 2D confined space of LDHs. Moreover, the tungsten content of 41.2 wt.% for the recycled catalyst is close to that of the fresh catalyst (42.3 wt.%), indicating the absence of leaching issues.

When the epoxidation reaction was half-way through (after 1h the conversion reached a value of 52 %), the Mg₃Al-ILs-La(PW₁₁)₂ was removed by filtration. The remaining reaction mixture kept under the same experimental conditions in the absence of the catalyst for 4h. Analysis of the reaction mixture revealed that no additional oxidation product was detected (Fig. 7b, red line). As soon as the solid Mg₃Al-ILs-La(PW₁₁)₂ was added back to the reaction mixture, the catalytic reaction resumed as expected.(Fig. 7b, black line). The experiment demonstrates that the Mg₃Al-ILs-La(PW₁₁)₂ is a truly efficient and robust heterogeneous catalyst, FT-IR (Fig. 7c), solid-state ²⁹Si cross-polarization magic-angle spinning (CP/MAS) NMR (Fig. 7d) and XPS spectra for the W_{4f} core level (Fig. S12), as well as the SEM, HRTEM images and EDX of the recycled Mg₃Al-ILs-La(PW₁₁)₂ (Fig. S13) suggest that the catalyst retains its morphology and structural integrity.

In order to evaluate the potential of the heterogeneous catalyst, we have focused our attention on the gram-scale synthesis of sulfoxide and epoxides. We have performed the selective oxidation of thioanisole and epoxidation of *cis*-cyclooctene reaction by scaling up the amount of substrate by a factor of 50. The scaled-up experiment reactions proceeded smoothly under the optimized experimental conditions. Using the selective oxidation of thioanisole as an example, we obtained excellent yields of the corresponding sulfoxides (96 %) with 99% selectivity under the optimized experimental conditions of 50 mmol thioanisole, 50 mmol H₂O₂, 10 ml CH₃OH, 1 g Mg₃Al-ILs-La(PW₁₁)₂, at 25 °C and 1h reaction time. The results demonstrate the potential of the designed heterogeneous catalyst for industrial applications.

Conclusions

In summary, a multicomponent heterogeneous catalyst Mg₃Al-ILs-La(PW₁₁)₂ was synthesized by adopting exfoliation/assembly approach. The grafting of ILs on the LDH not only induces flexibility to the catalyst but also allows easy access of the substrates to the active centre. The resultant catalyst shows high efficiency in the catalysis of various substrates such as the selective sulfoxidation of sulfides to sulfoxide, sulfones and epoxidation of olefins under mild conditions. The catalyst of Mg₃Al-ILs-La(PW₁₁)₂ can promote efficiently sulfoxidation reactions at 25 °C in 60 min with the conversion and selectivity remaining above 99 and 98 % respectively, producing 208 mmol g⁻¹ h⁻¹ of oxidation product. Additionally, it also can promote efficiently the epoxidation of *cis*cyclooctene at 70 °C in 5 h with the conversion and selectivity remaining above 97 and 99 % respectively, generating 31 mmol $g^{-1}h^{-1}$ of epoxides. Moreover, the structural stability of the Mg₃Al-ILs-La(PW₁₁)₂ composite is retained during the re-cycling process due to the multiple interactions between the three components (host layers, ILs and POMs). The Mg₃Al-ILs-La(PW₁₁)₂ composite can be separated easily from the reaction mixture by simple filtration and recycled at least five times without obvious decrease of its catalytic activity. Finally, the scaled-up experiment demonstrated the potential of the heterogeneous catalyst for industrial applications.

Experimental Section

Chemical Materials

All chemicals were of analytical grade and were used as received without any further purification. The [La(PW₁₁)₂],^[50] K₁₁[La(PW₁₁O₃₉)₂]·13H₂O Na₃PW₁₂O₄₀·15H₂O (PW₁₂),^[51] $K_6[P_2W_{18}O_{62}] \cdot 14H_2O$ (P₂W₁₈),^[52] [Mg_{0.75}Al_{0.25}(OH)₂](CO₃)_{0.125}·2H₂O (Mg₃Al-CO₃),^[53] [Mg_{0.75}Al_{0.25}(OH)₂](NO₃)_{0.25}·2H₂O (Mg₃Al-NO₃),^[54] 1octyl-3-(3-triethoxy-silylpropyl)-4,5-dihydro-imidazolium (ILs),^[55] Mg₃AI-ILs^[21] hexafluorophosphate were synthesized according to previously reported literature procedures.

Synthesis of Mg₃Al-ILs-La(PW₁₁)₂

Mg₃Al-NO₃ (0.3 g) was added into 300 mL of formamide in a three-necked flask purged with N₂. The mixture was vigorously stirred for 2 days. Then, the mixture was centrifuged for 10 min and the suspension was separated simply by filtration. Then, ILs (2.6 mmol) was dissolved in CH₃CN/CH₂Cl₂ (1:1, 5 mL) and added dropwise to the above isolated suspension. The reaction mixture was stirred under N₂ for 24 hours. The $K_{11}[La(PW_{11}O_{39})_2]$ ·13H₂O (1.68 g, La(PW_{11})_2) was dissolved in 30 mL formamide and added dropwise to the above solution. The precipitate of Mg₃Al-ILs-La(PW_{11})₂ (1.0 g) was collected by filtration and washed with ethanol, water and dried under vacuum overnight. Mg₃Al-ILs-PW₁₂ and Mg₃Al-ILs-P₂W₁₈ were obtained using similar procedure.

Catalytic test

In a typical sulfide oxidation experiment, a mixture of 1 mmol thioanisole, 1 mmol H₂O₂ (30 wt. %), 200 μ L CH₃OH and 20 mg catalyst Mg₃Al-ILs-La(PW₁₁)₂ (2.1 μ mol based on La(PW₁₁)₂) were added into a 10 mL glass bottle and the reaction mixture was kept under stirring at 25 °C. In a typical olefin epoxidation experiment, a mixture of 1 mmol *cis*-cyclooctene, 3 mmol H₂O₂ (30 wt. %), 1 mL CH₃CN and 40 mg catalyst Mg₃Al-ILs-La(PW₁₁)₂ (4.2 μ mol based on La(PW₁₁)₂) were added into a 10 mL glass bottle and the reaction mixture was kept under vigorous stirring at 70 °C. The resulting products were extracted with diethyl ether, analysed by GC and identified by ¹H-NMR and ¹³C-NMR in order to determine the selectivity and conversion.

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Entry for the Table of Contents

FULL PAPER

Exploitation of an exfoliation/assembly design approach led to the fabrication of an efficient heterogeneous catalyst for the selective sulfoxidation of sulfides and epoxidation of olefins. Synergistic effects between the catalyst's components led to high efficiency and selectivity for both types of reactions under mild conditions.



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Modular polyoxometalate-layered double hydroxides as efficient heterogeneous sulfoxidation and epoxidation catalysts