

# Facile immobilization of a Lewis acid polyoxometalate onto layered double hydroxides for highly efficient *N*-oxidation of pyridine based derivatives and denitrogenation

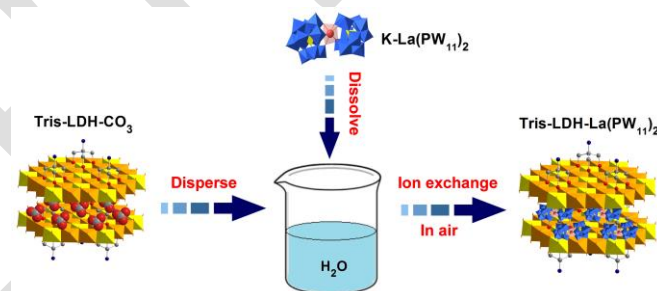
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**Abstract:** *N*-Oxides are a class of highly important compounds which are widely used as synthetic intermediates. In this paper, we demonstrate for the first time the use of a polyoxometalate (POM) based composite material, as highly efficient heterogeneous catalyst for the *N*-oxidation of pyridines and its derivatives in the presence of H<sub>2</sub>O<sub>2</sub> at room temperature. The composite was prepared by intercalation of the [La(PW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>11-</sup> anion into a tris(hydroxymethyl)aminomethane (Tris) modified layered double hydroxides (LDHs). Additionally, the Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>-based catalyst has been employed for the denitrogenation of a model oil mixture in the presence of [bmim]BF<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>. Deep denitrogenation can be achieved in 40 minutes at 75 °C. Finally, the heterogeneous catalyst can be easily recovered and reused at least ten times without measurable decrease of the catalytic activity and disintegration of the Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> structure.

heterogeneous catalysts including V<sub>x</sub>Si<sub>4x</sub>O<sub>6.4x</sub>,<sup>[15]</sup> GrO-MTO,<sup>[16]</sup> Ru(PVP)/c-Al<sub>2</sub>O<sub>3</sub>,<sup>[17]</sup> and Ti-MWW<sup>[18]</sup> were applied to the *N*-oxidation of pyridines. The drawbacks of these reported heterogeneous catalytic systems are the high reaction temperature and the poisonous organic solvents that are usually required for *N*-heterocycles that are resistant to oxidation due to their substantially higher oxidation potentials. Recently, it was shown that polyoxometalates (POMs) such as [(R<sub>4</sub>N)<sub>8</sub>][BW<sub>11</sub>O<sub>39</sub>H]<sup>[19]</sup> and [(C<sub>18</sub>H<sub>37</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>N]<sub>7</sub>[PW<sub>11</sub>O<sub>39</sub>]<sup>[20]</sup> are able to catalyse *N*-oxidation reactions. However, these systems exhibit issues with catalyst leaching and thermal stability. Consequently, there is great potential and of fundamental importance the development of efficient, recyclable and environmentally benign *N*-oxidation catalytic systems.

## Introduction

In recent years, heterocyclic *N*-oxides have received much attention due to their wide use as versatile synthetic intermediates, their biological importance, their use as protecting groups, auxiliary agents, oxidants, catalysts, surrogates for heterocyclic boronic acids and ligands in metal complexes.<sup>[1-4]</sup> It is known that the conventional preparation of pyridine *N*-oxides employs a non-catalytic oxidation process using dioxiranes,<sup>[5]</sup> activated H<sub>2</sub>O<sub>2</sub>,<sup>[6]</sup> H<sub>2</sub>SO<sub>5</sub> (Caro's acid)<sup>[7]</sup> and magnesium monophthalate<sup>[8]</sup> or peracids<sup>[9,10]</sup> as oxidants. However, these reagents not only are highly corrosive, but also generate large amounts of wastes during the reaction process which require frequent and laborious work-up treatments. In an effort to develop alternative synthetic routes and minimize the waste production of the *N*-oxidation process, research groups promoted the *N*-oxidation of pyridines using homogeneous catalysts including AcOH/H<sub>2</sub>O<sub>2</sub>,<sup>[11]</sup> MeReO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>,<sup>[12]</sup> trifluoroacetic anhydride (TFAA)/H<sub>2</sub>O<sub>2</sub><sup>[13]</sup> and Tf<sub>2</sub>O/Na<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O<sub>2</sub>.<sup>[14]</sup> Unfortunately, these homogeneous catalysts are not recyclable, which largely restrict their application in practice. In order to overcome such problems, a number of



**Scheme 1.** Representation of the synthetic process for the intercalation of [La(PW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>11-</sup> into Tris-stabilized LDHs.

In this paper, the catalytic efficacy of a lanthanum(III)-containing sandwich POM, K<sub>11</sub>[La(PW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>·15H<sub>2</sub>O] (denoted as K-La(PW<sub>11</sub>)<sub>2</sub>), has been evaluated for the *N*-oxidation of pyridine based substrates. The initial tests showed that the catalytic reaction proceeds efficiently under mild conditions (room temperature) in the presence of H<sub>2</sub>O<sub>2</sub> as oxidant. However, considering the cost and environmental impact associated with large scale applications, it is of fundamental importance to design and prepare a recyclable and reusable heterogeneous catalyst. It has been demonstrated that layered double hydroxides (LDHs) are excellent candidates for the immobilization of anionic POMs,<sup>[21-23]</sup> where the LDHs not only function as support, but also provide multiple interactions between the host layers and the guest POM anions. The intercalation of POMs into LDHs prevents the POM species from leaching into the reaction mixture whilst increases the selectivity of the catalytic reaction. Based on the above observations, we prepared a composite material based on the catalytically active [La(PW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>11-</sup> species by intercalating it into the Tris-modified LDHs (Tris = tris(hydroxyl)aminomethane).<sup>[24, 25]</sup> The heterogeneous catalyst of Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> shows

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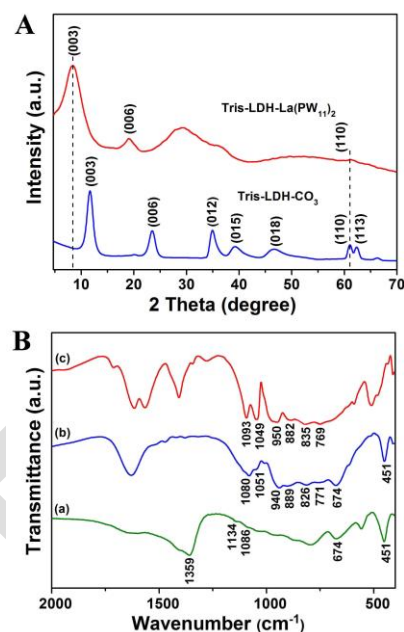
excellent catalytic activity on *N*-oxidations and denitrogenation reactions under mild conditions.

## Results and Discussion

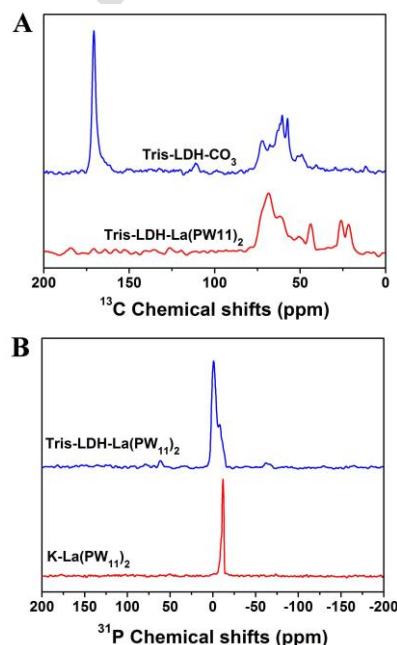
Ion exchange of K-La(PW<sub>11</sub>)<sub>2</sub> with Tris-LDH-CO<sub>3</sub> under ambient conditions without necessity of degassing CO<sub>2</sub> results in the formation of new intercalated assembly of Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> (Scheme 1). As shown in Figure 1, the XRD patterns of Tris-LDH-CO<sub>3</sub> show the characteristic (003), (006), (012), (110) and (113) at 2θ = 11.6°, 23.6°, 34.9°, 61.1°, and 62.3°, respectively. After ion exchange, the characteristic (003), (006), (012) of Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> shift to 8.9°, 19.5°, 29.4°, indicating that the [La(PW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>11-</sup> ions have been successfully intercalated into the interlayer of Tris-modified LDH.

FT-IR spectra of K<sub>11</sub>-La(PW<sub>11</sub>)<sub>2</sub>, Tris-LDH-CO<sub>3</sub> and Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> are presented in Figure 1B. For Tris-LDH-CO<sub>3</sub>, the peaks at 1086 cm<sup>-1</sup> and 1134 cm<sup>-1</sup> can be ascribed to the characteristic stretching vibration of M-O-C and C-C-O, respectively. For Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>, the asymmetric and symmetric vibration peaks at 1080 cm<sup>-1</sup> and 940 cm<sup>-1</sup> are assigned to the W-O stretching, while such vibration peaks appear at 1093 cm<sup>-1</sup> and 950 cm<sup>-1</sup> for K<sub>11</sub>-La(PW<sub>11</sub>)<sub>2</sub>. The red shift indicates the presence of strong electrostatic interactions and hydrogen bonding between the host layers and the guest POM anions.<sup>[26]</sup> The peak at 1051 cm<sup>-1</sup> can be assigned to the stretching vibration of P-O bond, which appears at 1049 cm<sup>-1</sup> in that of K<sub>11</sub>-La(PW<sub>11</sub>)<sub>2</sub>. The other characteristic peaks at 882 cm<sup>-1</sup>, 835 cm<sup>-1</sup>, 768 cm<sup>-1</sup> of K<sub>11</sub>-La(PW<sub>11</sub>)<sub>2</sub> can be due to the stretching vibration of W-O-W, which display at 889 cm<sup>-1</sup>, 826 cm<sup>-1</sup>, 771 cm<sup>-1</sup> in the spectrum of Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>, respectively. Additionally, the peak at 451 cm<sup>-1</sup> in both spectra of Tris-LDH-CO<sub>3</sub> and Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> is assigned to O-M-O vibration in the brucite-like layers of LDHs.<sup>[27]</sup> Meanwhile, the peak at 1359 cm<sup>-1</sup> of Tris-LDH-CO<sub>3</sub> due to the vibration of CO<sub>3</sub><sup>2-</sup> disappear in the spectrum of Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>, suggesting the successful ion exchange of CO<sub>3</sub><sup>2-</sup> by POM anions.

The <sup>13</sup>C CP/MAS NMR spectrum of Tris-LDH-CO<sub>3</sub> (Figure 2A) exhibits a strong signal at 171 ppm, which can be ascribed to the interlayer CO<sub>3</sub><sup>2-</sup> anions,<sup>[24]</sup> which is absent in the case of Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>, due to the complete ion exchange of the CO<sub>3</sub><sup>2-</sup> anions by the [La(PW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>11-</sup> anions during the intercalation process. Furthermore, one set of signals centered at δ = -5 ppm in the <sup>31</sup>P NMR spectrum of Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> implies that the [La(PW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>11-</sup> anions have been successfully incorporated in the Tris-modified LDHs (Figure 2B).



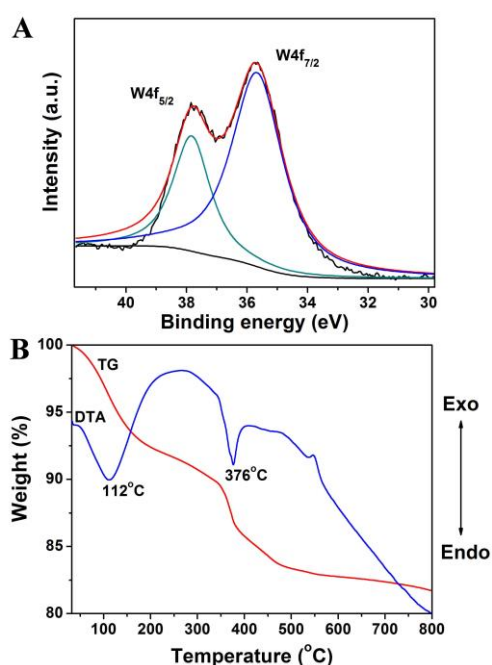
**Figure 1** (A) The XRD patterns of the Tris-LDH-CO<sub>3</sub> and Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>; (B) FT-IR spectra of (a) Tris-LDH-CO<sub>3</sub>, (b) Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> and (c) K<sub>11</sub>-La(PW<sub>11</sub>)<sub>2</sub>.



**Figure 2** (A) <sup>13</sup>C CP/MAS NMR spectra of Tris-LDH-CO<sub>3</sub> and Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>; (B) <sup>31</sup>P CP/MAS NMR spectra of Tris-LDH-CO<sub>3</sub> and Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>.

XPS analysis of the Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> is shown in Figure 3A. The W4f spectrum can be deconvoluted into doublets, which consist of W4f<sub>7/2</sub> at 35.6 eV and W4f<sub>5/2</sub> at 37.7 eV, respectively. The doublets are ascribed to the W in

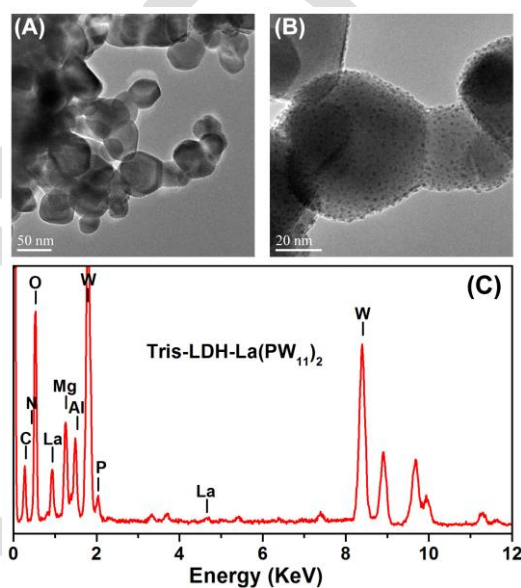
the W-O bond configuration and typically observed for  $W^{6+}$ .<sup>[28]</sup> This result is in accordance with the oxidation state of W element of K-La(PW<sub>11</sub>)<sub>2</sub>. TG-DTA analysis has been performed for the Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>. As shown in Figure 3B, two weight-loss stages can be observed with a temperature increase from 32 to 800 °C. The first weight loss is 8.29% between 40 and 244 °C, which can be ascribed to the removal of water molecules absorbed in the surface and interlayer space of Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>. The second weight loss step of 9.95% between 244-800 °C corresponds to the decomposition of Tris and the collapse of the layered structure. Based on the TG-DTA and elemental analysis results (Mg = 7.152%, Al = 3.969%, W = 54.41% and N = 0.588%), the elemental composition of the composite material can be identified as: Mg<sub>0.66</sub>Al<sub>0.33</sub>(C<sub>4</sub>H<sub>8</sub>NO<sub>3</sub>)<sub>0.093</sub>(OH)<sub>1.72</sub>La<sub>0.015</sub>(PW<sub>11</sub>O<sub>39</sub>)<sub>0.03</sub>·1.03H<sub>2</sub>O (Table S1).



**Figure 3** (A) XPS spectra for the W4f core level spectrum of the Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>; (B) TG-DTA of Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>.

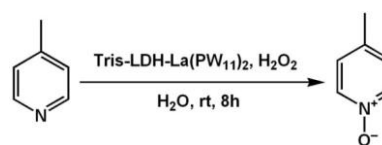
TEM images of the Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> (Figure 4) revealed that the material consists of 50–70 nm layered areas. The dark dots and blocks observed in the samples of Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> can be identified as the intercalated POM species. The acquired EDX data (Figure 4C) obtained from the black dots' regions observed in the TEM revealed the presence of La, P and W, consistent with the POM's composition of the molecular catalyst Tris-LDH-K<sub>11</sub>[La(PW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]. In addition, the size of the black spots falls in the range of 1-2 nm, which is in good agreement with the size of the POM clusters. Based on the above data, we have concluded that the black spots observed in TEM images are the POM anions. BET measurement has been

carried out on the Tris-LDH-CO<sub>3</sub> and Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>, in order to obtain more detailed information on the structural features of the as-prepared materials. The specific surface area, pore volume, and average pore diameter (estimated from N<sub>2</sub> adsorption–desorption isotherms) are presented in Table S2. Tris-LDH-CO<sub>3</sub> and Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> display H4 type hysteresis loops (Figure S1), indicating that the pores are produced by the aggregation of slit-shaped micro-sized pores,<sup>[29]</sup> which are similar to the conventional Mg<sub>3</sub>Al-POMs, but significantly different from the conventional Mg<sub>3</sub>Al-CO<sub>3</sub> which exhibits H3 type hysteresis loops.<sup>[30]</sup>



**Figure 4** (A), (B) TEM images of Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>; (C) EDX of Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>.

N-oxidation of pyridine and its derivatives:



**Scheme 2** The model reaction of *N*-oxidation of 4-picoline.

In order to evaluate the catalytic performance of Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>, we selected the oxidation of 4-picoline as a model reaction using 30 wt% H<sub>2</sub>O<sub>2</sub> as oxidant (Scheme 2). As shown in Table 1, the reaction proceeds efficiently in water in the presence of catalytic amount of Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> at room temperature and the corresponding 4-picoline-*N*-oxide can be obtained in high yields of ~95% (entry 6). In contrast, the Keggin POM of Na<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>]·15H<sub>2</sub>O (Na-PW<sub>12</sub>), the Dawson POM of K<sub>6</sub>[P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>]·19H<sub>2</sub>O (K-P<sub>2</sub>W<sub>18</sub>) and mono-lacunary Keggin P

OM of  $K_7[PW_{11}O_{39}] \cdot 13H_2O$  (K-PW<sub>11</sub>) provide yields of 72, 76 and 44%, respectively (entries 1-3). When  $La_2O_3$  and  $LaCl_3$  are used as catalysts, the reaction progress is sluggish (entries 4-5). It is noted that when K-La(PW<sub>11</sub>)<sub>2</sub> is applied to the reaction, 97% yields can be obtained, which is higher than 95% yields of Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>. This result is due to the fact that K-La(PW<sub>11</sub>)<sub>2</sub> is a highly efficient homogeneous catalyst while Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> is a heterogeneous catalyst where diffusion phenomena have considerable contribution. When Tris-LDH-CO<sub>3</sub> is used as catalyst on its own, a very low yield of 6% is obtained. Moreover, only H<sub>2</sub>O<sub>2</sub> without addition of catalyst results in only 12% oxidation of 4-picoline in water.

**Table 1** Oxidation of 4-picoline in water by different catalysts.<sup>[a]</sup>

Entry	Catalyst	Oxidant	Yield <sup>[b]</sup> (%)	TON <sup>[c]</sup>
1	Na-PW <sub>12</sub>	H <sub>2</sub> O <sub>2</sub>	72	180
2	K-P <sub>2</sub> W <sub>18</sub>	H <sub>2</sub> O <sub>2</sub>	76	190
3	K-PW <sub>11</sub>	H <sub>2</sub> O <sub>2</sub>	44	110
4	La <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	31	78
5	LaCl <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	17	43
6	K-La(PW <sub>11</sub> ) <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	97	243
7	Tris-LDH-CO <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	6	15
8	Tris-LDH- La(PW <sub>11</sub> ) <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	94	235
9	No	H <sub>2</sub> O <sub>2</sub>	12	-

[a] Reaction conditions: 1 mmol 4-picoline, 5 mmol (30 wt%) H<sub>2</sub>O<sub>2</sub>, 4 μmol catalyst, 1 mL H<sub>2</sub>O, room temperature, 8 h. Assignments of products were analysed using <sup>1</sup>H NMR and <sup>13</sup>C NMR. [b] Isolated yields. [c] TON = molar of product/molar of catalyst used.

**Table 2** Oxidation of 4-picoline<sup>[a]</sup> with H<sub>2</sub>O<sub>2</sub> mediated in different solvents.<sup>[b]</sup>

Entry	Solvent	Yield <sup>[c]</sup> (%)	TON <sup>[d]</sup>
1	Methanol	12	30
2	Ethanol	15	38
3	Acetone	4	10
4	Acetonitrile	8	20
5	Ethyl acetate	52	130
6	Toluene	81	203
7	Trichloromethane	42	105
8	Water	94	235

[a] 4-picoline is readily soluble in all solvent systems. [b] Reaction conditions: 1 mmol 4-picoline, 5 mmol (30 wt%) H<sub>2</sub>O<sub>2</sub>, 4 μmol catalyst of Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>, 1 mL solvent, room temperature, 8 h. Assignments of products were analysed using <sup>1</sup>H NMR and <sup>13</sup>C NMR. [c] Isolated yields. [d] TON = molar of product/molar of catalyst used.

Investigation of the influence of the solvents on the oxidation reaction (Table 2) shows that the oxidation reaction gives relatively low yields of 12%, 15%, 4%, 8% in methanol, ethanol, acetone, acetonitrile, respectively. Meanwhile, the oxidation reaction gives relatively higher yields of 52%, 81%, 42%, 94% in ethyl acetate, toluene, trichloromethane and water. The different yields could be attributed to the different interactions between 4-picoline and the solvents and the different solubility of 4-picoline in various solvents. Thus, the optimized solvent for the model reaction is water.

In an effort to test the general applicability of the composite's catalytic efficacy on this type of reaction, a series of pyridine derivatives are subjected to the optimized

reaction conditions. As shown in Table 3, most of the substrates can be successfully oxidized to the corresponding *N*-oxides in high yields at room temperature. The obtained data demonstrate that the pyridine could be oxidized to pyridine-*N*-oxide within only 4 h at 99% yield. As for the mono- or di-methyl substituted pyridine substrates such as 2-picoline, 3-picoline, 4-picoline and 2,3-lutidine, 2,6-lutidine, 96%, 95%, 94% and 93%, 92% yield can be obtained within 6-8 h respectively, (entries 2-6). For the electron deficient substrate of 2-chloropyridine, the *N*-oxidation process exhibits a relatively low yield of 24% (entry 7). Furthermore, the quinoline can be successfully oxidized to the corresponding quinoline-*N*-oxide with a yield of 91% in 4h at 65°C (entry 8). Isoquinoline and 8-hydroxyquinoline can also be efficiently oxidized to corresponding products at slightly elevated temperatures (65 °C).

**Table 3** Oxidation of pyridines with H<sub>2</sub>O<sub>2</sub> by Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> in water.<sup>[a]</sup>

Entry	Substrat	Product	<i>t</i> (h)	Yield <sup>[b]</sup> (%)	TON <sup>[c]</sup>
1			4	99	248
2			6	96	240
3			6	95	238
4			8	94	235
5			8	93	233
6			8	92	230
7			16	24	60
8 <sup>c</sup>			4	91	228
9 <sup>c</sup>			4	92	230
10 <sup>c</sup>			4	98	245

[a] Reaction conditions: 1 mmol substrate, 5 mmol (30 wt%) H<sub>2</sub>O<sub>2</sub>, 4 μmol catalyst of Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>, 1 mL H<sub>2</sub>O, room temperature. Assignments of products were analysed using <sup>1</sup>H NMR and <sup>13</sup>C NMR. [b] Isolated yields. [c] TON = molar of product/molar of catalyst used.

Denitrogenation by Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>:

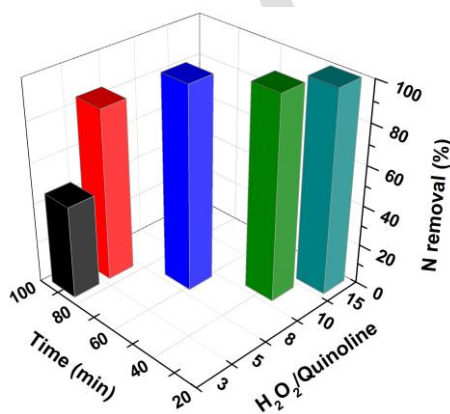
Petrochemical streams contain, amongst to a series of mono/and polyaromatic compounds, N/S-containing heterocyclic species. Considering the environmental impact

of these components and the induced problems in numerous refinery processes, the industries employ various processes (denitrogenation and desulphurization) for their removal. Thus, we made an effort to investigate our heterogeneous catalyst's efficacy under experimental conditions used in refinery processes. More specifically, we investigated the efficacy of the Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> heterogeneous catalyst in the denitrogenation processes. Initially, we studied the oxidation of quinoline in model oil at different temperatures (Table 4) in order to identify the effect of the temperature on the denitrogenation process. It is observed that 53%, 59%, 66% and 78% nitrogen removal can be achieved at 25, 35, 45 and 55 °C, respectively, in 90 min. A further temperature increase to 65 or 75 °C leads to almost 100% denitrogenation of quinoline in 55 and 40 min, respectively. Therefore, we use the temperature of 75 °C for the subsequent experiments.

**Table 4** Effect of temperature on nitrogen removal by the Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>/[bmim]BF<sub>4</sub> system at 75 °C.<sup>[a]</sup>

Entry	T (°C)	t (min)	N removal (%)
1	25	90	53
2	35	90	59
3	45	90	66
4	55	90	78
5	65	55	100
6	75	40	100

[a] Reaction conditions: 122 µL H<sub>2</sub>O<sub>2</sub>, 17 mL model oil (N content 100 ppm), 1 mL [bmim]BF<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>/quinoline/Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> = 300:30:1.



**Figure 5** Effect of H<sub>2</sub>O<sub>2</sub>/quinoline molar ratio on nitrogen removal of quinoline. Reaction conditions: T = 75 °C, 17 mL model oil (N content 100 ppm), 1 mL [bmim]BF<sub>4</sub>, quinoline/ Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> = 30:1.

The optimum amount of H<sub>2</sub>O<sub>2</sub> for the the N-oxidation of the removed N-containing compounds has been identified in a series of control experiments by applying different H<sub>2</sub>O<sub>2</sub>/quinoline molar ratios under the experimental conditions of T = 75 °C, N = 100 ppm and quinoline/Tris-

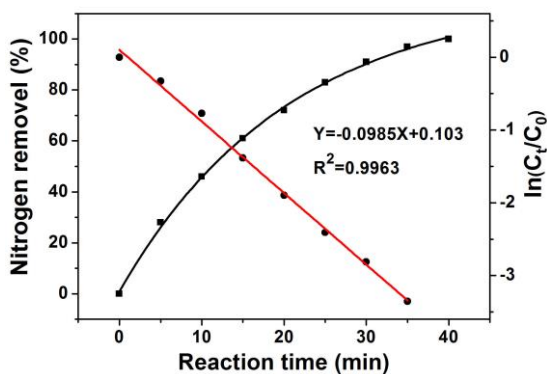
La(PW<sub>11</sub>)<sub>2</sub> = 30:1. Upon increasing the H<sub>2</sub>O<sub>2</sub>/quinoline molar ratio from 3:1 to 5:1 (Figure 5), the nitrogen removal increases from 46% to 85% in 90 min. When the molar ratio is increased to 8:1, 100% nitrogen removal can be achieved in 65 min. A further increase of the H<sub>2</sub>O<sub>2</sub>/quinoline ratio to 10:1 or 15:1 leads to deep denitrogenation in only 40 or 30 min, respectively. Therefore, the selected H<sub>2</sub>O<sub>2</sub>/quinoline ratio for our subsequent experiments is the optimized value of 10:1.

**Table 5** Effect of quinoline/Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> molar ratio on nitrogen removal by Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub>/[bmim]BF<sub>4</sub> system at 75 °C.<sup>[a]</sup>

Entry	H <sub>2</sub> O <sub>2</sub> /Quinoline/Cat	H <sub>2</sub> O <sub>2</sub> (µL)	t (min)	N removal (%)
1	600:60:1	122	90	100
2	600:60:2=300:30:1	122	40	100
3	600:60:4=150:15:1	122	50	100
4	600:60:8=150:15:2	122	40	96
5	600:60:8=150:15:2	122	60	100
6	900:60:1	183	70	100
7	900:60:2=450:30:1	183	30	100
8	900:60:4=450:30:2	183	30	100
9	900:60:8=450:30:4	183	30	100

[a] Reaction conditions: T = 75 °C, 17 mL model oil (N = 100 ppm), 1 mL [bmim]BF<sub>4</sub>,

Further investigation of the quinoline/Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> molar ratios on the nitrogen removal process has been carried out at 75 °C. As shown in Table 5, the time for deep denitrogenation increases from 40 to 90 min when the quinoline/Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> molar ratio decreases from 60:2 to 60:1 in the presence of H<sub>2</sub>O<sub>2</sub> (entry 1). It can be found that when quinoline/Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> molar ratio reaches to 60:4 and 60:8, nitrogen removal reaches 100% in 50 min and 60 min, respectively. Furthermore, slight increase of the amount of H<sub>2</sub>O<sub>2</sub> to 0.183 mL leads to almost 100% denitrogenation removal in only 30 min at 75 °C with the H<sub>2</sub>O<sub>2</sub>/quinoline/Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> molar ratio of 900:60:8 (entry 9).

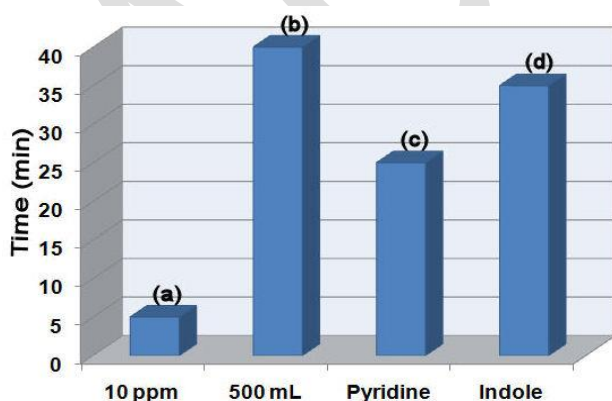


**Figure 6** Nitrogen removal of quinoline and  $\ln(C_t/C_0)$  as a function of the reaction time at 75 °C.  $\text{H}_2\text{O}_2 = 0.122$  mL, 17 mL model oil ( $N = 100$  ppm),  $[\text{bmim}]\text{BF}_4 = 1$  mL,  $\text{H}_2\text{O}_2/\text{quinoline}/\text{Tris-LDH-La}(\text{PW}_{11})_2 = 300:30:1$ .

The nitrogen removal percentage and the  $\ln(C_t/C_0)$  are plotted against the reaction time in Figure 6, where  $C_0$  and  $C_t$  are the initial quinoline concentration and quinoline concentration at time  $t$ , respectively. The linear fit of the data reveals that the catalytic reaction exhibits pseudo-first-order kinetics for the denitrogenation of quinoline ( $R^2 = 0.9959$ ). The rate constant  $k$  of the oxidation reaction was determined to be  $0.0985 \text{ min}^{-1}$  on the basis of Equations (1) and (2). Oxidation of quinoline to quinoline- $N$ -oxide can be completed in 40 min. Thus, the catalyst exhibits high efficiency for oxidation of quinoline to quinoline- $N$ -oxide, and the catalytic reaction obeys pseudo-first-order kinetics with 100% selectivity for quinoline- $N$ -oxide.

$$-\frac{dC_t}{dt} = k \quad (1)$$

$$\ln\left(\frac{C_0}{C_t}\right) = kt \quad (2)$$

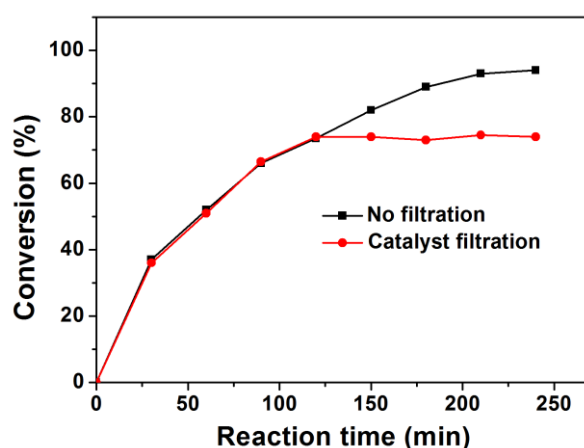


**Figure 7** Nitrogen removal of a) quinoline (10 ppm, 17 mL), b) quinoline (100 ppm, 500 mL), c) pyridine (100 ppm, 17 mL) and d) indole (100 ppm, 17 mL). Reaction conditions:  $T = 75$  °C, a) 17 mL model oil = 17 mL ( $N = 10$  ppm),  $\text{H}_2\text{O}_2/\text{quinoline}/\text{Tris-LDH-La}(\text{PW}_{11})_2 = 300:3:1$ ; b) 500 mL model oil ( $N = 100$

ppm),  $\text{H}_2\text{O}_2/\text{quinoline}/\text{Tris-LDH-La}(\text{PW}_{11})_2 = 300:30:1$ ; c) 17 mL model oil ( $N = 100$  ppm),  $\text{H}_2\text{O}_2/\text{pyridine}/\text{Tris-LDH-La}(\text{PW}_{11})_2 = 300:30:1$ ; d) 17 mL model oil ( $N = 100$  ppm),  $\text{H}_2\text{O}_2/\text{indole}/\text{Tris-LDH-La}(\text{PW}_{11})_2 = 300:30:1$ .

As shown in Figure 7, with the  $N$  content as low as 10 ppm, 100 % nitrogen removal can be achieved in only 8 min under mild conditions. With an increase in the volume of model oil to 500 mL, deep denitrogenation can be completed in 40 min. The result shows that high efficiency denitrogenation for different substrates including pyridine, quinoline and indole can be achieved in the presence of the  $\text{Tris-LDH-La}(\text{PW}_{11})_2 / [\text{bmim}]\text{BF}_4$  system. The time required for 100% nitrogen removal of pyridine, quinoline and indole is 25, 40 and 35 min, respectively. Thus, the denitrogenation activity decreases in the order of pyridine > indole > quinoline, in agreement with the electron density on the nitrogen atoms of the aromatic ring and steric hindrance considerations.

To confirm the catalyst is truly heterogeneous,  $N$ -oxidation of 4-picoline has been carried out using  $\text{Tris-LDH-La}(\text{PW}_{11})_2$  as catalyst and  $\text{H}_2\text{O}_2$  as oxidant at 25 °C in water. The catalyst was separated from the reaction mixture when the conversion was 80% at the reaction time of 125 mins. The GC monitoring of the reaction mixture showed that the substrate's conversion immediately stops. Addition of the filtered catalyst back to the reaction mixture, re-initiates the reaction the conversion reaches 99% (Figure 8). Furthermore, the catalyst was separated from the reaction mixture by centrifugation, washed with water and reused for at least 10 times without obvious loss of its activity (Figure S2). Moreover, the structure of  $\text{Tris-LDH-La}(\text{PW}_{11})_2$  remains intact after the  $N$ -oxidation reaction, as evidenced by FT-IR, XRD,  $^{13}\text{P}$  NMR and XPS spectra (Figure S2). The above data confirm further that the catalysis of  $\text{Tris-LDH-La}(\text{PW}_{11})_2$  is truly heterogeneous.



**Figure 8** The recycling and reuse experiment demonstrates the heterogeneous nature of the  $\text{Tris-LDH-La}(\text{PW}_{11})_2$  catalyst.

The suggested mechanism for the denitrogenation of the oil phase and consequent catalytic oxidation of 4-picoline in the aqueous phase by Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> in the presence of H<sub>2</sub>O<sub>2</sub> is represented Figure 9. The substrate of 4-picoline is firstly extracted by the ionic liquid of [bmim]BF<sub>4</sub> to the aqueous phase since [bmim]BF<sub>4</sub> is water soluble. The intermolecular interaction at the interphase of the two solvent systems promotes the extraction process. Based on the N-containing products in the oil stream the nature of the ionic liquid can vary accordingly.<sup>[31-34]</sup> The presence of H<sub>2</sub>O<sub>2</sub> and POM component of the Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> catalyst promote the formation of POM-based peroxy species responsible for the oxygen transfer and subsequent oxidation of the substrate to the corresponding 4-picoline-N-oxide compound. The ability of oxygen transfer *via* the generation of peroxy species in polyoxometalate systems is well known and has been studied extensively by various groups previously.<sup>[35-37]</sup>



**Fig 9.** The proposed mechanism for the denitrogenation of the oil phase and consequent catalytic oxidation of 4-picoline in the aqueous phase by Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> in the presence of H<sub>2</sub>O<sub>2</sub>.

## Conclusions

To summarize, we have successfully prepared a Lewis acid POM-intercalated Tris-modified LDHs composite material. The resulting nanocomposite Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> has been fully characterized by various techniques. Furthermore, Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> has been investigated as heterogeneous catalyst for the *N*-oxidation of pyridines and denitrogenation of model oil. Notably, the *N*-oxidation of pyridines to the corresponding *N*-oxides can be easily achieved at room

temperature with an excellent selectivity, high yield and high efficiency. Deep denitrogenation can be achieved within 40 min at 75 °C. In addition, the catalyst can be easily recovered and recycled for more than 10 times without obvious loss of catalytic activity. Therefore, the catalyst has shown a great potential for practical and industrial application.

## Experimental Section

**Chemical materials:** Quinoline (99%), pyridine (99%), indole (99%), 2-picoline (98%), 3-picoline (99%), 4-picoline (99%), 2,3-lutidine (98%), 2,6-lutidine (99%), 2-chloropyridine (99%), isoquinoline (99%), 8-hydroxyquinoline (99%), *n*-octane (98%), hydrogen peroxide (30 wt% H<sub>2</sub>O<sub>2</sub>) and the ionic liquids [bmim]BF<sub>4</sub>, (bmim = 1-butyl-3-methylimidazolium) were purchased from *Sigma-Aldrich* and used directly without further purification. All solvents were of analytical grade, purchased from *Alfa Aesar* and used without further purification.

**Characterization:** Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku XRD-6000 diffractometer under the following conditions: 40 kV, 30 mA, Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm). FT-IR spectra were recorded on a Bruker Vector 22 infrared spectrometer using KBr pellets. The solid state NMR experiments were carried out at 75.6 MHz for <sup>13</sup>C and at 121.0 MHz for <sup>31</sup>P on a Bruker Avance 300M solid-state spectrometer equipped with a commercial 5 mm MAS NMR probe. The N<sub>2</sub> adsorption-desorption isotherms were measured using a Quantachrome Autosorb-1 system at the liquid nitrogen temperature, and the samples were degassed at 120 °C for 6 hours before the measurements. TEM images were conducted on a JEOL JEM-2010 electron microscope operating at 200 kV. Thermogravimetric and differential thermal analyses (TG-DTA) were performed on a TGA/DSC 1/1100 SF from Mettler Toledo in flowing N<sub>2</sub> with a heating rate of 10 °C min<sup>-1</sup> from 32 °C to 800 °C. X-ray photoelectron spectroscopy (XPS) measurements were performed with monochromatized Al K $\alpha$  exciting X-radiation (PHI Quantera SXM). An inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Shimadzu ICPS-7500) was used to measure the concentration of W in the catalysts. GC analyses were performed with an Agilent 7820A GC system using a 30 m 5% phenylmethyl silicone capillary column with an ID of 0.32 mm and 0.25 mm coating (HP-5).

Tris-LDH-CO<sub>3</sub> was prepared according to the reference.<sup>[24]</sup> The catalyst was synthesized by ion exchange method as reported.<sup>[25]</sup>

**Oxidation of pyridines to *N*-oxides:** 1 mmol substrate, 30 wt% H<sub>2</sub>O<sub>2</sub> aqueous solution, 0.4 mol% catalyst (Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> contain POMs 4  $\mu$ mol) and 1 mL H<sub>2</sub>O were mixed in a 20 mL glass bottle at 25 °C or 65 °C and the reaction mixture was kept under vigorous stirring. The reactions were effectively quenched after 4-12 h. The resulting organic

products were separated from the aqueous phase by extraction and the extracts were analysed by gas chromatography with a flame ionization detector (GC-FID). The conditions were as follows: injection port temperature 290 °C; detector temperature 290 °C; oven temperature 70 °C; carrier gas: ultrapure nitrogen; sample injection volume 1 mL.

Denitrogenation of model oil: In a typical experiment, a solution of quinoline, pyridine, and indole in n-octane was used as model oil with an N content of 100 ppm. The catalytic oxidative denitrogenation experiments were performed in a 25 mL two-necked flask, to which 0.122 mL of 30 wt% H<sub>2</sub>O<sub>2</sub>, 17 mL of model oil, 1 mL of [bmim]BF<sub>4</sub>, and Tris-LDH-La(PW<sub>11</sub>)<sub>2</sub> (H<sub>2</sub>O<sub>2</sub>/quinoline/Cat = 300 : 30 : 1) were added. The reaction mixture was stirred at 75 °C. During the reaction, the upper layer of the model-oil phase was periodically withdrawn and analysed by gas chromatography with a flame ionization detector (GC-FID). Quinoline, pyridine and indole were identified using reference standards.

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**Key words:** polyoxometalates • layered double hydroxides • N-oxidation • denitrogenation • heterogeneous catalyst

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