Polyoxometalate-Intercalated Layered Double Hydroxides as Efficient and Recyclable Bifunctional Catalysts for Cascade Reactions

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The polyoxometalate (POM) intercalated layered double hydroxides (LDHs) have been widely used as heterogeneous catalysts. However, the application of POM–LDHs as bifunctional catalysts for cascade reaction has seldom been studied compared to the noble-metal-based catalysts. Herein, a series of POM–LDHs catalysts of Tris–LDH–X₄(PW₉)₂ (X=Mn, Fe, Co, Ni, Cu, and Zn; Tris=Tris(hydroxymethtyl)aminomethane) have been prepared. The efficacy of Tris–LDH–Zn₄(PW₉)₂ as efficient bifunctional catalyst has been demonstrated for cascade reac-

Introduction

One-pot cascade reactions have attracted the interest of organic synthetic chemists in recent years,^[1-4] as they can drastically simplify complex synthetic pathways and reduce the production wastes and energy consumption.^[5-9] A feasible route for the efficient progression of cascade reactions is based on the design of new catalysts with spatially isolated multiple active sites, which can promote simultaneously different reactions. To date, a wide variety of catalytic systems have been proposed for cascade reactions, however, many of these are based on homogeneous catalysts.^[10,11] In contrast to homogeneous catalysts, their heterogeneous counterparts exhibit significant advantages such as facile recovery and recyclability, least possible contamination of the reaction medium, as well as high stability. Although the catalytic efficacy of heterogeneous catalysts such as Au/TiO₂,^[12] Au-Pd/resin,^[13] Pd/MOF^[14] and Pt/polymer^[15] etc. in cascade reactions has been demonstrated, the incorporation of noble-metal centers, the addition of soluble base, and the use of high-temperature regimes are generally required to achieve high yields of the target product in

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are available on the WWW under http://dx.doi.org/10.1002/ cctc.201501365. tions involving oxidation of benzyl alcohol to benzaldehyde followed by Knoevenagel condensation with ethyl cyanoacetate to produce benzylidene ethyl cyanoacetate. The combination of POM's redox/acidic sites and LDHs's basic sites led to a composite catalyst with excellent activity (99%) and selectivity (\geq 99%) under mild and soluble-base-free conditions. This work offers a new design strategy for the fabrication of efficient bifunctional catalysts for the promotion of one-pot cascade reactions.

a reasonable timescale. Therefore, the development of highly efficient noble-metal-free heterogeneous catalysts for one-pot cascade reactions without additives (e.g., base) under mild conditions is highly demanding, although it is challenging as well.

Polyoxometalates (POMs) are a large class of discrete metal oxide clusters of early transition metals such as V, Mo, and W, etc., which have been widely applied in catalytic reactions,^[16] such as oxidation of alcohols,^[17-19] epoxidation of alkenes and alkenols,^[20,21] bromination of alkenes,^[22,23] and water splitting.^[24,25] Layered double hydroxides (LDHs)^[26] are a series of layered materials with tunable interlayer galleries, with the general formula of $[M^{2+}_{1-x}M^{3+}_{x}(OH)_{2}](A^{n-})_{x/n} \cdot m H_{2}O$, in which M^{2+} and M^{3+} are di- and trivalent metal cations, and A^{n-} is a counter anion. It has been demonstrated that LDHs are effective supports for the immobilization of anionic POM catalysts.^[27-30] Indeed, LDHs possess a number of active basic sites that can efficiently catalyze Knoevenagel condensation reactions.^[31-33] Hence, it is highly desirable to design new bifunctional POM-LDHs catalysts, which can promote both oxidation and Knoevenagel condensation reactions in the absence of any other additives under mild conditions.

In this work, we report the preparation of a series of bifunctional catalysts of the general formula Tris-LDH-X₄(PW₉)₂ (Tris = Tris(hydroxymethyl)aminomethane, X = Mn, Fe, Co, Ni,and Zn) intercalating POM Cu by anions of $[X_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (X = Mn, Fe, Co, Ni, Cu, and Zn) into a Tris-modified LDH using a facile ion exchange method. Among all the members of this family of catalysts, Tris-LDH-Zn₄(PW₉)₂ exhibits the highest activity and selectivity in the cascade reaction of oxidation-Knoevenagel condensation between benzyl alcohol and ethyl cyanoacetate to produce benzylidene ethyl cyanoacetate under mild and soluble-base-free



conditions. Finally, the heterogeneous catalysts can be easily recovered and reused for at least ten times without obvious deterioration of their structural integrity and activity attributable to the strong host–guest interaction between the LDHs and POM anions.

Results and Discussion

Synthesis and Characterization

Ion exchange of $K-X_4(H_2O)_2(PW_9O_{34})_2$ with Tris-LDH-CO₃ under ambient conditions without the necessity of degassing CO₂ led to the formation of a new intercalated assembly of Tris-LDH- $X_4(PW_9)_2$ (Scheme 1). As revealed in Figure 1A, the XRD patterns of Tris-LDH-CO₃ show the characteristic peaks for the (003), (006), (012), (110), and (113) lattice planes at $2\theta =$



Scheme 1. Schematic representation of the synthetic process for the intercalation of $[Zn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ into Tris-stabilized LDHs. Color code: yellow and light blue octahedral = MgO₆ or AlO₆, red and gray spheres = Tris, dark blue and green octahedral = WO₆ and ZnO₆.



Figure 1. A) XRD patterns of a) Tris–LDH–CO₃ and b–g) Tris–LDH–X₄(PW₉)₂ (X = Mn, Fe, Co, Ni, Cu, and Zn, respectively), B) FT-IR spectra of a) Tris–LDH–CO₃, (b) Tris–LDH–Zn₄(PW₉)₂, c) K[Zn₄(H₂O)₂(PW₉O₃₄)₂]^{10–}.

11.5, 23.5, 34.8, 61.1, and 62.4°, respectively. After ion exchange, the characteristic peaks for the (003) and (006) planes of Tris–LDH–X₄(PW₉)₂ shift to 8.5° and 18.3°, indicating that the $[X_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ ions have been successfully intercalated into the interlayer of Tris–modified LDH.

The FT-IR spectrum of $K_{10}[Zn_4(H_2O)_2(PW_9O_{34})_2]$ in Figure 1B, which is denoted K-Zn₄(PW₉)₂ in the rest of the manuscript, exhibits peaks at 939, 887, and 745 cm⁻¹, which are attributed to the vibrations of W–O_t, W–O_c–W, and W–O_e–W (t, terminal; c, corner sharing; e, edge sharing),^[34] respectively. These W-O stretching bands can be clearly observed in the FT-IR spectrum of Tris-LDH-Zn₄(PW₉)₂ slightly shifted to 941, 891 and 748 cm⁻¹, respectively. The observed shift is the result of the strong electrostatic interactions and hydrogen bonds formed between the layers of LDHs and the POM anions.^[38] The peak at 1034 cm⁻¹ in both spectra of K–Zn₄(PW₉)₂ and Tris–LDH– $Zn_4(PW_9)_2$ can be assigned to the P–O vibration of the heteroatom within the POM clusters. Additionally, the absorption bands in the range of 400-800 cm⁻¹ in both spectra of Tris-LDH-CO3 and Tris-LDH-Zn4(PW9)2 are attributed to O-M-O vibrations in the brucite-like layers of LDHs.^[35] Remarkably, the peak at 1359 cm⁻¹ of Tris-LDH-CO₃, attributed to the vibration of CO₃²⁻ anions, disappears in the FT-IR spectrum of the composite Tris-LDH-Zn₄(PW₉)₂, suggesting the successful ion exchange of CO3²⁻ anions by POM clusters. The FT-IR spectra of Tris-LDH-X4(PW9)2 (X = Mn, Fe, Co, Ni and Cu) are shown in Figure S1 in the Supporting Information.

Additional evidence of the complete exchange of the CO₃^{2–} anions can be seen from the ¹³C cross-polarization magic-angle-spinning (CPMAS) NMR study of Tris and Tris–LDH–CO₃ (Figure 2 A). The spectrum exhibits a strong signal at 171.1 ppm, which can be ascribed to the interlayer CO₃^{2–} anions.^[35] Notably, this signal is absent in the ¹³C CPMAS NMR spectrum of Tris–LDH–Zn₄(PW₉)₂ composite material indicative of the complete ion exchange of the CO₃^{2–} anions by the [Zn₄(H₂O)₂(PW₉O₃₄)₂]^{10–} anions during the intercalation process. Furthermore, one set of signals centered at $\delta = -4.6$ ppm can be observed in the ³¹P NMR spectrum of Tris–LDH–Zn₄(PW₉)₂ and K–Zn₄(PW₉)₂, indicating that the POM anions have been successfully incorporated into the Tris-modified LDHs (Figure 2 B).

XPS analysis of the composite $Tris-LDH-Zn_4(PW_9)_2$ is shown in Figure 3. Initial survey of the XPS spectrum showed that the Tris-LDH-Zn₄(PW₉)₂ sample is composed of the elements of Mg, Al, Zn, P, and W (Figure 3A). In Figure 3B-C, the relevant binding energies of Mg1s (1303.5 eV) and Al2p (74.4 eV) attributed to the presence of the Tris-modified LDH are presented, and in Figure 3D-F the peaks of the relevant binding energies of Zn 2p, P 2p, and W4f resulting from the intercalation of the $[Zn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ clusters in the Tris–LDH–Zn_4(PW_9)_2 composite material are shown. Furthermore, the W4f spectrum (Figure 3F) can be deconvoluted into a doublet consisting of $W4f_{\scriptscriptstyle 7/2}$ at 35.7 eV and $W4f_{\scriptscriptstyle 5/2}$ at 37.8 eV, respectively. The doublet is ascribed to the W in the W-O-bond configuration and typically can be assigned to the existence of W⁶⁺ centers.^[39] This result is in agreement with the oxidation state of the W centers originating from the starting material, $K-Zn_4(PW_9)_2$.



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Figure 2. A) ^{13}C CPMAS NMR spectra of Tris, Tris–LDH–CO₃, and Tris–LDH– $Zn_4(PW_9)_2$, (B) ^{31}P CPMAS NMR spectra of K– $Zn_4(PW_9)_2$ and Tris–LDH– $Zn_4(PW_9)_2$.

Thermogravimetric differential thermal analysis (TG–DTA) was performed for the Tris–LDH– $Zn_4(PW_9)_2$ sample, and two weight-loss stages were observed as the temperature in-

creased from 32 to 800 °C (Figure 4 A). The first weight loss of 7.23% occurs between 40 and 244 °C, which can be attributed to the removal of water molecules absorbed in the surface and the interlayer space of the Tris–LDH–Zn₄(PW₉)₂ composite. The second weight-loss step of 8.74% at 244–800 °C corresponds to the decomposition of Tris molecules and subsequent disin-



Figure 4. A) TG–DTA of Tris–LDH– $Zn_4(PW_9)_2$ and B) adsorption–desorption isotherms of Tris–LDH– CO_3 , Tris–LDH– $Zn_4(PW_9)_2$. The inset shows the pore size distribution of Tris–LDH– CO_3 and Tris–LDH– $Zn_4(PW_9)_2$.



Figure 3. A) XPS spectra of the Tris-LDH-Zn₄(PW₉)₂ sample and deconvolution of the peaks for B) Mg 1s, C) Al 2p, D) Zn 2p, E) P 2p, F) W 4f.



tegration of the layered structure. Based on the TG–DTA and elemental analysis considerations (Mg=8.071%, AI=4.483%, W=54.692%, and N=0.644%), the elemental composition of the composite material can be identified as: Mg_{0.66}Al_{0.33}(C₄H₈NO₃)_{0.092}(OH)_{1.71}Zn_{0.132}(PW₉O₃₄)_{0.066}·0.87 H₂O (Supporting Information, Table S1). The TG analysis plots of K–Zn₄(PW₉)₂ and Tris–LDH–CO₃ are shown in Figure S2 for comparison.

BET measurements were performed on the Tris–LDH–CO₃ and Tris–LDH–Zn₄(PW₉)₂ samples to obtain more detailed information on the structural features of the as-prepared material. The specific surface area, pore volume, and average pore diameter (estimated from N₂ adsorption–desorption isotherms) are reported in Table S2. Tris–LDH–CO₃ and Tris–LDH–Zn₄(PW₉)₂ display H4-type hysteresis loops (Figure 4B), indicating that the pores are produced by the aggregation of slit-shaped microsized pores.^[40]

SEM analysis (Figure S2) shows that the plate sizes of Tris– LDH–Zn₄(PW₉)₂ are in the range of approximately 20–30 nm. High-resolution (HR) TEM images of the Tris–LDH–Zn₄(PW₉)₂ are shown in Figure 5. The observed homogeneously distribut-



Figure 5. A–C) HRTEM images of Tris–LDH–Zn₄(PW₉)₂ at different magnification, D) EDX analysis of Tris–LDH–Zn₄(PW₉)₂.

ed dark dots of approximately 1 nm diameter size in the samples of Tris–LDH– $Zn_4(PW_9)_2$ can be ascribed to the intercalated POM species. Energy-dispersive X-ray (EDX) spectrometric studies (Figure 5 D) conducted on the dark areas identified from the HRTEM images revealed the presence of Mg, Al, Zn, P, W, C, and N, which provides further support for the composition of the Tris–LDH– $Zn_4(PW_9)_2$.

The CO₂ temperature-programmed desorption (CO₂ TPD) measurement of Tris–LDH–Zn₄(PW₉)₂, Mg₂Al–Zn₄(PW₉)₂, and Zn₂Al–Zn₄(PW₉)₂ are outlined in Figure 6. All these samples display three kinds of CO₂ desorption peaks, which can be ascribe to weak basic sites centered at 90–153 °C, moderate basic sites centered at 164–227 °C, and strong basic sites ranging from

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Figure 6. CO2 TPD curves of a) $Zn_2Al-Zn_4(PW_9)_2,$ b) $Mg_2Al-Zn_4(PW_9)_2,$ and c) Tris–LDH– $Zn_4(PW_9)_2.$

252 to 373 °C. In comparison with Mg₂Al–Zn₄(PW₉)₂ and Zn₂Al–Zn₄(PW₉)₂, Tris–LDH–Zn₄(PW₉)₂ contains larger amount of basic sites, particularly of the stronger ones. Notably, Tris–LDH–Zn₄(PW₉)₂ has a much higher basic-site density than Mg₂Al–Zn₄(PW₉)₂ and Zn₂Al–Zn₄(PW₉)₂ based on the data summarized in Table 1, and Zn₂Al–Zn₄(PW₉)₂ possesses the lowest basic-site density among the three samples.

Table 1. Results of temperature-programmed desorption of CO_{2} for the studied samples.						
Sample specific basicity $[CO_2 \mu mol g^{-1}]^{[a]}$						
	total	W.	М.	S.		
Zn ₂ Al–Zn ₄ (PW ₉) ₂	248	146.5 (59.1) ^[b]	54.7 (23.0)	46.8 (18.9)		
Mg ₂ Al–Zn ₄ (PW ₉) ₂	305	158.3 (51.9)	13.6 (4.5)	133.1 (43.6)		
Tris-LDH-Zn ₄ (PW ₉) ₂	614	134.1 (21.8)	12.3 (2.0)	467.6 (76.2)		
[2] W : work basic sites: M : moderate basic sites: S : strong basic sites						

[a] W.: weak basic sites; M.: moderate basic sites; S.: strong basic sites. [b] Relative amounts of the basic sites (%).

Cascade catalytic reaction

The performance and efficacy of the Tris–LDH–Zn₄(PW₉)₂ composite as a bifunctional heterogeneous catalyst was tested in the conversion of benzyl alcohol (**A1**) to benzylidene ethyl cyanoacetate (**C1**) in an one-pot cascade reaction. The cascade reaction involves two separate steps: 1) oxidation of benzyl alcohol to benzaldehyde (**B1**) by POM anions in the presence of H₂O₂ and 2) Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate promoted by the basic sites of the LDHs. The catalytic performance of a series of control experiments was also investigated for comparison and the results are summarized in Table 2.

The cascade reaction proceeds smoothly with 99% conversion and \geq 99% selectivity using the Tris-LDH-Zn₄(PW₉)₂ catalyst (Table 2, entry 6). The control samples of Tris-LDH-X₄(PW₉)₂ (X = Mn, Fe, Co, Ni, and Cu) show considerably lower conversion of **A1** (entries 1–5), indicating that the POM anions hosted in the Tris-modified LDH play an important role for the efficient oxidation of **A1** during the first step of the reaction. If Mg₂Al-



Table 2. Performance of different catalysts in the oxidation of benzyl alcohol and the subsequent Knoevenagel condensation with ethyl cyanoacetate. $^{\rm [a]}$

CHO LDH CODEL							
А	.1 E	31		C1			
Entry	Catalyst	Conv. A1 [%]	Yield B1 [%]	Yield C1 [%]	TON ^[b]		
1	Tris-LDH-Mn ₄ (PW ₉) ₂	12	0	12	12		
2	Tris-LDH-Fe ₄ (PW ₉) ₂	20	0	20	20		
3	Tris-LDH-Co ₄ (PW ₉) ₂	29	0	29	29		
4	Tris-LDH-Ni ₄ (PW ₉) ₂	25	0	25	25		
5	Tris-LDH-Cu ₄ (PW ₉) ₂	47	0	47	47		
6	Tris-LDH-Zn ₄ (PW ₉) ₂	99	0	99	99		
7	$Mg_2AI - Zn_4(PW_9)_2$	95	13	82	82		
8	Zn ₂ Al–Zn ₄ (PW ₉) ₂	94	33	61	61		
9	$K-Zn_4(PW_9)_2$	100	92	8	8		
10	Tris-LDH-CO ₃	trace	trace	trace	trace		
11	$K - Zn_{4}(PW_{9})_{2} +$	83	31	52	52		
	Tris-LDH-CO ₃						
12 ^[c]	Pd/Zeolites	87	48	39	-		
13 ^[d]	Zr-MOF-NH ₂	100	2	98	-		
14	none	0	0	0	-		
[a] Reaction conditions: catalyst (0.01 mmol), A1 (1 mmol), ethyl cyano- acetate (3 mmol), H_2O_2 (1 mL), CH_3CN (3 mL), $T=353$ K, 6 h. [b] TON= moles of product C1 per moles of catalyst used. [c] Ref. [41]: $T=358$ K, 15 h. [d] Ref. [42]: $T=363$ K, 48 h.							

 $Zn_4(PW_9)_2$ and $Zn_2AI-Zn_4(PW_9)_2$ are used instead, the relevant conversion values for A1 found to be nearly the same as that for Tris-LDH-Zn₄(PW₉)₂; however, the relevant yields regarding the condensation step towards the formation of C1 are found to be significantly lower (entries 7, 8) owing to the lower basicity of the conventional LDH support than that observed in Trismodified LDH. Notably, Zn₂Al-Zn₄(PW₉)₂ exhibits a much lower yield for C1 than Mg₂Al-Zn₄(PW₉)₂ because of the lower basicity of the former composite. Investigation of the catalytic efficacy of the monofunctional catalysts reveals that neither K- $Zn_4(PW_9)_2$ nor Tris-LDH-CO₃ can convert A1 into the target product C1 (entries 9, 10). Finally, the physical mixture of Tris-LDH–CO₃ and K–Zn₄(PW₉)₂ with comparable active site concentrations shows inferior efficacy (entry 11), as both the activity and selectivity are considerably lower than those observed for the bifunctional catalyst $Tris-LDH-Zn_4(PW_9)_2$, demonstrating the advantages of the proposed POM-intercalated catalyst design. In comparison with Tris-LDH-Zn₄(PW₉)₂, the reported Pd/zeolites^[41]-based catalyst exhibits a much lower conversion and lower selectivity for the same cascade reaction. Moreover, the performance of the $Zr-MOF-NH_2$ (MOF = metal-organic framework) catalyst,^[42] for the same cascade reaction found to be quite sluggish.

To identify the best solvent medium for the cascade reaction, we investigated the effects of a series of solvents on the catalytic efficacy; the results are summarized in Table 3. The cascade reaction proceeds efficiently if CH₃OH and C₂H₅OH are used as solvents with the conversion of **A1** reaching 93% and 92%, respectively (entries 1, 2). If CH₃CN is used, we observe almost complete conversion of **A1** (99%) and selectivity for

Table 3. Effect of different solvents on the oxidation of benzyl alcohol and the subsequent Knoevenagel condensation with ethyl cyanoacetate $^{\left[a\right] }$

Entry	Solvent	Conv. A1 [%]	Yield B1 [%]	Yield C1 [%]	TON ^[b]	
1	CH₃OH	93	0	93	93	
2	C₂H₅OH	92	0	92	92	
3	CH₃CN	99	0	99	99	
4	THF	78	16	62	62	
5	toluene	84	9	75	75	
6	DMF	89	4	85	85	
7	DMSO	66	12	44	44	
8	H ₂ O	47	8	39	39	
[a] Reaction conditions: Tris–LDH–Zn ₄ (PW ₉) ₂ (0.01 mmol), A1 (1 mmol), ethyl cyanoacetate (3 mmol), H_2O_2 (1 mL), solvent (3 mL), $T=353$ K, 6 h. [b] TON = moles of product C1 /moles of catalyst used.						

the final product, **C1** (100%). In contrast, the catalytic activity and selectivity decrease dramatically if THF, toluene, DMF, DMSO, and H₂O are used as solvents in the cascade reaction (entries 4–8). Based on the above screening, we selected CH₃CN as the most appropriate solvent medium.

The catalytic reaction pathway was explored by tracing the product distribution change as a function of the reaction time using Tris–LDH– $Zn_4(PW_9)_2$ as the catalyst. In Figure 7 A, the evolution with time of the different products is shown for the reaction of benzyl alcohol and ethyl cyanoacetate in the presence of the bifunctional catalyst. Initially, the benzaldehyde can be obtained through oxidation of benzyl alcohol by the



Figure 7. A) Reaction profile of oxidation–Knoevenagel condensation reaction of benzyl alcohol and ethyl cyanoacetate. a) A1 (black), b) B1 (red), c) C1 (blue). B) Kinetic study for the conversion of A1 with Tris–LDH– Zn₄(PW₉)₂. Reaction conditions: Tris–LDH–Zn₄(PW₉)₂ (0.01 mmol), A1(1 mmol), ethyl cyanoacetate (3 mmol), H₂O₂ (1 mL), solvent (3 mL), T=353 K, 6 h.



POM clusters in the presence of H_2O_2 . Simultaneously, in the presence of the basic sites of Tris-modified LDH, ethyl cyanoacetate is activated to give a nucleophile, which rapidly condenses with benzaldehyde leading to the formation of the condensation product, benzylidene ethyl cyanoacetate. It should be noted that the yield of benzaldehyde increases initially as a function of the reaction time and then decreases slowly after 1 h owing to subsequent conversion to the condensation product (**C1**), which is a typical behavior for a tandem reaction. The schematic reaction profile is illustrated in Scheme 2.

The kinetic study for conversion of **A1** by Tris–LDH– Zn₄(PW₉)₂ is illustrated in Figure 7 B. The percentage of conversion and $\ln(C_t/C_0)$ are plotted against the reaction time, in which C_0 and C_t are the initial **A1** concentration and the concentration at time *t*, respectively. The linear fit of the data demonstrates that the catalytic reaction exhibits pseudo-first-order kinetics for the conversion of **A1** ($R^2 = 0.9956$). The rate con-



Scheme 2. Reaction pathway of the oxidation–Knoevenagel condensation reaction catalyzed by Tris–LDH–Zn₄(PW₉)₂. Color code: yellow and light blue octahedral = MgO₆ or AlO₆, dark blue and green octahedral = WO₆ and ZnO₆, gray and red spheres = Tris.

stant k of the conversion of A1 can be determined to be 0.7661 h^{-1} .

$$-\frac{dC_t}{dt} = k \tag{1}$$

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

In an effort to test the general applicability and efficacy of the Tris-LDH-Zn₄(PW₉)₂ heterogeneous catalyst in cascade reactions involving different substrates, we have studied the conversion of a series of substituted benzyl alcohols (A) and active methylene compounds (B); the obtained results are summarized in Table 4. The data demonstrate that the introduction of electron donor groups at the para position of the benzyl alcohol leads to high yields of the target product (C) (Table 4, entries 2-4) after prolonged reaction time; on the other hand, electron-withdrawing groups at the para position exhibit decreased yields for the final condensation product (C) (entries 5-8). Specifically, for 2,6-difluorobenzyl alcohol, a much lower conversion of A and selectivity for C is observed (entry 9), which can be attributed to the net electron-withdrawing effect and the increased steric hindrance of the bulky groups in A. If malononitrile is used as the condensation reactant, the whole cascade reaction proceeds fast to completion within 4 h (entry 10). On the contrary, the yields for the final product (C) are moderately to significantly lower for of diethyl malonate and phenylacetonitrile, respectively (entries 11, 12). Malononitrile is the most active methylene compound among the substrates used in this work, which is reflected in the observed differences in the yields for C in the cascade reaction.

To evaluate the stability of the composite material, identify potential leaching issues, and demonstrate the heterogeneous nature of the Tris–LDH– $Zn_4(PW_9)_2$ composite material, we designed the following experimental procedure. After allowing

$R^{1} \frown OH \xrightarrow{POM} R^{1} \frown \frac{LDH}{R^{2} \frown R^{3}} R^{1} \frown \frac{R^{2}}{R^{3}}$								
			А	В	С			
Entry	R ¹	R ²	R³	t [h]	Conv. A1 [%]	Yield B1 [%]	Yield C1 [%]	TON ^[b]
1	C ₆ H ₅	CN	COOEt	6	99	0	99	99
2	4-CH ₃ -C ₆ H ₅	CN	COOEt	16	92	0	92	92
3	4-CH ₃ O-C ₆ H ₅	CN	COOEt	24	93	0	93	93
4	$4-NH_2-C_6H_5$	CN	COOEt	24	90	0	90	90
5	4-F-C ₆ H ₅	CN	COOEt	24	86	0	86	86
6	4-CI-C ₆ H ₅	CN	COOEt	24	83	0	83	83
7	4-Br-C ₆ H ₅	CN	COOEt	24	79	0	79	79
8	$4-NO_2-C_6H_5$	CN	COOEt	24	60	0	60	60
9	2,6-2F-C ₆ H ₅	CN	COOEt	24	48	16	32	32
10	C ₆ H ₅	CN	CN	4	99	0	99	99
11	C ₆ H ₅	COOEt	COOEt	16	99	7	92	92
12	C ₆ H ₅	C_6H_5	CN	24	99	25	64	64
[a] Reaction conditions: Tris-LDH-Zn ₄ (PW ₅) ₂ (0.01 mmol), alcohol (1 mmol), active methylene compounds (3 mmol), H_2O_2 (1 mL), CNCH ₃ (3 mL), $T = 353$ K.								

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the benzyl alcohol and ethyl cyanoacetate to react for 2 h, we removed the catalyst from the reaction vessel by filtration while the conversion of benzyl alcohol and the yield of the condensation product at this point reached 72% and 58%, respectively (Figure 8A). The reaction mixture was kept under



Figure 8. A) Leaching test for the cascade reaction of benzyl alcohol with ethyl cyanoacetate over Tris–LDH–Zn₄(PW₉)₂. a) conversion of benzyl alcohol, b) yield of benzylidene ethyl cyanoacetate. Reaction conditions: benzyl alcohol (1 mmol), ethyl cyanoacetate (1.5 mmol), H₂O₂ (1 mL), solvent (3 mL), catalyst (0.01 mmol), T=353 K. B) Recycling test of the Tris–LDH–Zn₄(PW₉)₂ catalyst for 10 times.

stirring for another 4 h under the same experimental conditions while we kept monitoring any concentration changes of the species. The obtained data (Figure 8A) demonstrate that the removal of the solid catalyst, Tris-LDH-Zn₄(PW₉)₂ from the reaction mixture, brings the cascade reaction, and as a consequence the conversion of benzyl alcohol and the yield of the target product, to a halt. In addition, inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements of the filtrate after removing the catalyst indicate no evidence of W content in the filtrate. These two experimental results provide unambiguous proof that there is no leaching of POM clusters from the Tris-LDH-Zn₄(PW₉)₂ composite into the solution during the course of the cascade reaction. This can be attributed to the multiple electrostatic and H-bonding interactions between Tris-modified LDH and POM anions in the twodimensionally restricted region.

Most importantly, the heterogeneous catalyst can be successfully recovered upon completion of the cascade reaction by filtration. As shown in Figure 8B, the Tris–LDH– $Zn_4(PW_9)_2$ composite used for the promotion of the cascade reaction can be easily recovered by filtration and recycled for at least 10 times without obvious deterioration of its catalytic activity. In addition, the characterization of the recycled catalyst using

XRD, FT-IR, ³¹P NMR, and XPS analyses demonstrate the retention of its structural integrity (Figure S4).

Conclusions

A series of bifunctional catalysts of the general formula Tris-LDH- $X_4(PW_9)_2$ (X = Mn, Fe, Co, Ni, Cu, and Zn; Tris = tris(hydroxymethyl)aminomethane; LDH = layered double hydroxides) have been fabricated by intercalating the polyoxymetalate (POM) anions into Tris-modified LDH following a facile ion exchange method. The experimental results show for the first time the efficient utilization of POM-LDH composite materials as bifunctional heterogeneous catalysts for the promotion of cascade reactions. The combinatorial effect of this family of composite materials was demonstrated by the fine-tuning of the oxidation catalyst (POM) and the basicity of the LDH layers (Knoevenagel condensation). More specifically, the Tris-LDH-Zn₄(PW₉)₂ composite exhibited excellent activity and selectivity under mild and soluble-base-free conditions in the cascade oxidation-Knoevenagel condensation reaction of various substituted benzyl alcohol and active methylene substrates. This work demonstrates the POM-intercalated LDHs as very attractive low cost, energy-efficient and noble-metal-free alternative catalysts. Moreover, the reported heterogeneous catalysts can be easily recovered upon completion of the cascade reaction and recycled for at least ten times without measurable deterioration of their catalytic activity or structural integrity. This new approach opens up endless possibilities for the engineering of low-cost, environmentally friendly and modular multifunctional POM-LDH catalysts, tailored for the promotion of specific cascade reactions. Our current research effort is focused on exploring the potential of the family of POM-LDHs-based multifunctional catalysts.

Experimental Section

Chemicals

MgCl₂·6H₂O, AlCl₃·6H₂O, Zn(NO₃)₂·6H₂O, MnCl₂·2H₂O, FeCl₃·6H₂O, Co(NO₃)₂·6H₂O, Ni(NO₃)₃·6H₂O, CuCl₂·2H₂O, Al(NO₃)₃·9H₂O, Na₂CO₃, NaWO₄·2H₂O, H₃PO₄, CH₃COOH, KCl, tris(hydroxymethyl)aminomethane (Tris), benzyl alcohol, 4-methylbenzyl alcohol, 4-methoxybenzyl alcohol, 4-fluorobenzyl alcohol, 4-chlorobenzyl alcohol, 4-bromobenzylalcohol, 4-aminobenzyl alcohol, 4-nitrobenzyl alcohol, 2,6-difluorobenzyl alcohol, ethyl cyanoacetate, malononitrile, diethyl malonate, and phenylacetonitrile were purchased from *Sigma-Aldrich* and used without any further purification. All solvents were of analytical grade, purchased from Alfa Aesar and used without further purification.

Preparation of the catalysts

Tris–LDH–Zn₄(PW₉)₂: K₁₀[Zn₄(H₂O)₂(PW₉O₃₄)₂]·20H₂O^[34] (K–Zn₄(PW₉)₂) and the tripodal-ligand-stabilized layered double hydroxide (Tris–LDH–CO₃)^[35] were synthesized according to previously reported methodologies. The POMs were intercalated into Tris–LDH–CO₃ using an anion-exchange method^[36] under CO₂-existing conditions. Tris–LDH–CO₃ (2 mg mL⁻¹) was then redispersed in a solution of K₁₀[Zn₄(H₂O)₂(PW₉O₃₄)₂] (0.1 M) and stirred for 2 h at RT. The precipi-



tate was then filtered, washed with water and acetone, and dried in an oven to obtain the Tris–LDH–Zn₄(PW₉)₂ composite.

Tris–LDH–X₄(PW₉)₂ (X=Mn, Fe, Co, Ni, Cu), Mg₂Al-Zn₄(PW₉)₂, and Zn₂Al-Zn₄(PW₉)₂: Tris–LDH–X₄(PW₉)₂ (X=Mn, Fe, Co, Ni, Cu) were fabricated following the synthetic procedure according to the literature.^[34–36] Mg₂Al–CO₃ and Mg₂Al–NO₃,^[37] Mg₂Al–Zn₄(PW₉)₂,^[30] and Zn₂Al–CO₃ and Zn₂Al–NO₃,^[29] were synthesized according to previously reported literature methods.

One-pot oxidation-Knoevenagel condensation reaction

Solid catalyst (0.01 mmol), benzyl alcohol (1 mmol), ethyl cyanoacetate (1.5 mmol), 30 wt % H_2O_2 aqueous solution (1 mL), and acetonitrile (3 mL) were mixed in a 20 mL glass bottle at 80 °C and the reaction mixture was kept under vigorous stirring. The reaction mixtures were effectively quenched after 6 h by H_2O (5 mL). The resulting oily products were extracted with diethyl ether and analyzed by gas chromatography equipped with a flame ionization detector (GC–FID). The conditions were as follows: injection port temperature 340 °C; detector temperature 340 °C; oven temperature 70 °C; carrier gas: ultrapure nitrogen; sample injection volume 1 mL.

Characterization

Powder 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 performed at 75.6 MHz for ¹³C and at 121.0 MHz for ³¹P on a Bruker Avance 300 м solid-state spectrometer equipped with a commercial 5 mm MAS NMR probe. The N₂ 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 h before the measurements. HRTEM images were conducted on a JEOL JEM-2010 electron microscope operating at 200 kV. SEM images were obtained using a Zeiss Supra 55 SEM. TG-DTA was performed on a TGA/DSC 1/1100 SF from Mettler Toledo in flowing N₂ with a heating rate of 10°C min⁻¹ from 32°C to 800°C. XPS measurements were performed on a PHI Quantera SXM using monochromatized $AI_{K\alpha}$ exciting X-radiation. The basicity of the composites were probed by the temperature-programmed desorption of carbon dioxide (CO₂ TPD) using a Thermo Electron Corporation TPDRO 1100 analyzer. The samples (100 mg) were degassed by heating at 100 °C for 2 h under a He stream (50 mL min⁻¹) and then treated with CO₂ stream (40 mLmin⁻¹) at 50 °C for 1 h. Physically adsorbed CO₂ was removed by a flushing He stream at the saturation temperature for 2 h. Chemisorbed CO₂ was desorbed by heating from the saturation temperature up to 600°C at a rate of 10°C min⁻¹. ICP-AES (Shimadzu ICPS-7500) was used to measure the concentration of W in the catalysts. GC analyses were performed on an Agilent 7820 A 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).

Acknowledgements

This work was supported by National Basic Research Program (2014CB932104), National Science Foundation of China (U1407127), the Fundamental Research Funds for the Central Universities (RC1302, YS1406, XK1530) and Beijing Engineering Centre for Hierarchical Catalysts. H.N.M acknowledges the financial support from University of Glasgow, Royal Society of Edinburgh and Marie Curie actions scheme.

Keywords: heterogeneous catalysts · intercalations · layered compounds · polyoxometalates · transition metals

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Received: December 15, 2015 Published online on January 26, 2016