Tailoring the Synergistic Bronsted-Lewis acidic effects in Heteropolyacid catalysts: Applied in Esterification and Transesterification Reactions

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In order to investigate the influences of Lewis metals on acidic properties and catalytic activities, a series of Keggin heteropolyacid (HPA) catalysts, $H_nPW_{11}MO_{39}$ ($M = Ti^{IV}, Cu^{II}, Al^{III}, Sn^{IV}, Fe^{III}, Cr^{III}, Zr^{IV}$ and $Zn^{II}$; for Ti and Zr, the number of oxygen is 40), were prepared and applied in the esterification and transesterification reactions. Only those cations with moderate Lewis acidity had a higher impact. Ti Substituted HPA, $H_5PW_{11}TiO_{40}$, posse lower acid content compared with $Ti_{1-x}H_3PW_{12}O_{40}$ ($Ti$ partial exchanged protons in saturated $H_3PW_{12}O_{40}$), which demonstrated that the Lewis metal as an addenda atom ($H_5PW_{11}TiO_{40}$) was less efficient than those as counter cations ($Ti_{1-x}H_3PW_{12}O_{40}$). On the other hand, the highest conversion reached 92.2% in transesterification and 97.4% in esterification. Meanwhile, a good result was achieved by $H_5PW_{11}TiO_{40}$ in which the total selectivity of DAG and TGA was 96.7%. In addition, calcination treatment to $H_5PW_{11}TiO_{40}$ make it insoluble in water which resulted in a heterogeneous catalyst feasible for reuse.

Heteropolyacids (HPAs) with Keggin structure are friendly acid catalysts for various organic reactions1–4. In this context, Lewis acidic HPAs have been synthesized through partial exchange of protons with metal cations5–7. Sn-exchanged $Sn_{0.75}H_{0.25}PW_{12}O_{40}$ has been studied in different reactions including the selective hydrolysis of cellulose to glucose8,9, cyanosilylation of ketones and aldehydes10, esterification or transesterification9,11, and Friedel-Crafts alkylation reactions5,9. Zhu's group developed a high active Ag-exchanged HPA (Ag$_x$H$_{1-x}$PW$_{12}$O$_{40}$) for the glycerol esterification with acetic acid14. N. Lingaiah et al. reported the ZnPW$_{12}$O$_{40}$ catalyst for the synthesis of glycerol carbonate from glycerol and urea, the high efficiency was attributed to the incorporation of Zn$^{2+}$ into the secondary structure of heteropolytungstate15. Up to now, only one report had been reported concerning the acidic properties of $H_nPW_{11}MO_{39}$ ($M = Ti, Zr$ and $Th$)16. Other transition metal mono-substituted $PW_{11}O_{39}$ (Lewis metals include Ti$^{IV}$, Cu$^{II}$, Al$^{III}$, Sn$^{IV}$, Fe$^{III}$, Cr$^{III}$, Zr$^{IV}$ and Zn$^{II}$) have rarely been studied systematically. The focus of our paper is to determine how substituted metals affect the acidic property and catalytic activity of $H_nPW_{11}MO_{39}$. Meanwhile, as one of the most studied processes for evaluation of catalytic activity, esterification between alcohols and organic acids is of great interest in academical and industrial fields. In this case, we selected the esterification of glycerol with acetic acid, which also has an environmental and industrial importance in biomass conversion, as a model reaction to investigate the influence of Lewis center on the catalytic activity. In addition, we also studied the effects of Lewis metals on transesterification. Among

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all, $H_5PW_{11}TiO_{40}$ was the most active, water-tolerant and acid-tolerant HPAs. Calcination treatment to $H_5PW_{11}TiO_{40}$ made it insoluble in water which confirmed its heterogeneous performance in both esterification and transesterification.

Success of this work might clarify the different effects of Lewis metals on total acidity of HPAs and provide more information on how to select proper HPAs according to different requirements.

Methods

Material and reagent. All the chemicals were of AR grade, which were obtained commercially and used without further purification. $Na_7PW_{11}O_{39}$ was synthesized according to the ref. 17.

Instrument. Elemental analysis was carried out using a Leeman Plasma Spec (I) ICP-ES and a PE 2400 CHN elemental analyzer. IR spectra ($4000–500 \text{ cm}^{-1}$) was recorded in KBr discs on a Nicolet Magna 560 IR spectrometer. The IR spectra of adsorbed pyridine (Py-IR) were depicted by subtracting the spectra before and after exposure to pyridine. X-ray diffraction (XRD) patterns of the sample were collected on a Japan Rigaku Dmax 2000 X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.154178 \text{ nm}$). SEM micrographs were recorded on a scan electron microscope (XL30 ESEM FEG 25 kV). The concentrations of esters were determined periodically on Shimazu GC-14C fitted with a HP-INNO Wax capillary column $(30 \text{ m} \times 0.25 \text{ mm})$ and flame ionization detector. Each of the catalytic reaction was repeated for three times.

Catalyst preparation. $K_5PW_{11}TiO_{40}$ was synthesized according to the procedure described previously. Firstly, Ti ($SO_4$)$_2$ solution (6 mmol in 2 M $H_2SO_4$) was added to the aqueous solution of $Na_7PW_{11}O_{39}$ (6 mmol). Then, adjusting the pH of the mixture to 5.6 by $NaHCO_3$, followed by adding solid KCl (2.24 g) until white precipitate, $K_5PW_{11}TiO_{40}$, was formed. After that, the precipitate was filtrated and recrystallized with water for three times. Other catalysts were synthesized as following: firstly, 29.4 g (100 mmol) $Na_2WO_4$ and 1.29 g (9.1 mmol) $Na_2HPO_4$ were dissolved in 80 mL deionized water at room temperature under vigorous stirring. Secondly, 20 mL metal salts aqueous solution (12 mmol) (chlorides for Sn; nitrates for Fe, Cr and Zn; sulfate for Al, Cu and $ZrO_2\cdot xH_2O$) was added dropwise to the former solution with continuous stirring. After that, 100 mL deionized water was added additionally. The pH was adjusted to 5.6 by $HNO_3$, then KCl (3.39 g) was added until the precipitate formed. This precipitate was filtrated and recrystallized with water for three times giving potassium salt of $KPW_{11}M$ ($M = Ti^{IV}, Cu^{II}, Al^{III}, Sn^{IV}, Fe^{III}, Cr^{III}, Zr^{IV}$ and $Zn^{II}$).

2 g potassium salts of $KPW_{11}M$ ($M = Ti^{IV}, Cu^{II}, Al^{III}, Sn^{IV}, Fe^{III}, Cr^{III}, Zr^{IV}$ and $Zn^{II}$) were dissolved respectively in 1000 mL deionized water and the potassium cations were replaced by $H^+$ using strong-acid cation exchange resins (Type 732, 20 g) for several times to give HPW$_{11}M$, until no $K^+$ can be detected by ICP analysis. Then the HPW$_{11}M$ solution was rotary evaporated at 50°C to remove water and give powders. These powders were calcinated for 3h at 200°C to obtain insoluble products. The formation of HPW$_{11}M$ undergoes the following equations:

$$11WO_4^{4−} + HPO_4^{−2} + 17H^+ → [PW_{11}O_{39}]^{7−} + 9H_2O \quad (1)$$

$$[PW_{11}O_{39}]^{7−} + M^{x+} + (9 - x)K^+ + H_2O → K_{9−x}PW_{11}MO_{40} + 2H^+ \times (M = Ti^{IV} \text{ and } Zr^{IV}) \quad (2)$$

$$[PW_{11}O_{39}]^{7−} + M^{x+} + (9 - x)K^+ → K_{9−x}PW_{11}MO_{39} \times (M = Cu^{II}, Al^{III}, Sn^{IV}, Fe^{III}, Cr^{III}, Zr^{IV} \text{ and } Zn^{II}) \quad (3)$$

$$K_{9−x}PW_{11}MO_{40} + (9 - x)H^+ → H_{9−x}PW_{11}MO_{40} \times (M = Ti^{IV} \text{ and } Zr^{IV}) \quad (4)$$

$$K_{9−x}PW_{11}MO_{39} + (9 - x)H^+ → H_{9−x}PW_{11}MO_{39} \times (M = Cu^{II}, Al^{III}, Sn^{IV}, Fe^{III}, Cr^{III}, Zr^{IV} \text{ and } Zn^{II}) \quad (5)$$

Determination of the acidic properties. Titration was used to evaluate the total acid content of the solids. 0.05 g HPW$_{11}M$ suspended in 45 mL acetonitrile and then the mixture was stirred for 3h. The density of acid sites in the catalysts was measured by titration with a solution of n-butylamine in acetonitrile (0.05 M) using the indicator anthraquinone ($pK_a = −8.2$). The IR spectra of adsorbed pyridine (Py-IR) helped to measure the acid content and distinguish the properties of acid sites (Lewis or Brønsted). The samples were exposed to the pyridine vapor for 12 h under vacuum ($10^{-3}$ Pa) at 60°C. The quantification of acidity was calculated by Lambert–Beer equation:
where $A$ is the absorbance (area in cm$^{-1}$), $\varepsilon$ is the extinction coefficient (m$^2$/mol), $W$ is the sample weight (kg), $c$ is the concentration of acid (mol/kg or mmol/g) and $S$ is the sample disk area (m$^2$), respectively.

The amount of Brønsted and Lewis acid sites was estimated from the integrated area of the adsorption bands at ca. 1540 and 1450 cm$^{-1}$, respectively, using the extinction coefficient values based on the previous report$^{21}$.

### Esterification reaction.

A 25 mL three-necked glass flask equipped with a water-cooled condenser was charged with glycerin (2.3 g, 25 mmol), different volume of acetic acid and certain amount of catalyst. Each mixture was vigorously stirred and reacted at desired temperature for the required reaction time. After the reaction, the mixture was rotary evaporated at 55°C to remove the excess acetic acid. The products, the unreacted glycerol and the solid catalyst were left in the reactor. Then the catalyst was separated by centrifuging, washed with water, and calcinated at 100°C for reuse. The liquid mixture was tested by GC. In addition, we have checked the mixture before and after rotary evaporator by GC which confirmed that there was no additional reaction because the time (1 min) was too short to allow any additional reactions occur. The conversion of glycerol and selectivity of glycerides were calculated by the following equations:

$$
Conversion(\%) = \frac{\text{moles of glycerol (in)} - \text{moles of glycerol (out)}}{\text{moles of glycerol (in)}} \times 100\%
$$

$$
Selectivity(\%) = \frac{\text{moles of one product}}{\text{moles of all products}} \times 100\%
$$

### Transesterification reaction.

1.88 mL glycerol triacetin was added to a 25 mL three-necked glass flask with ethanol-cooled condenser (the temperature is $-3\,^\circ C$) under vigorous stirring. After being preheated to 65°C, the specified amount of methanol (molar ratio of oil/methanol was 1: 6) and 4 wt% of catalyst was added under stirring at 300 rpm to keep the system uniform in temperature and suspension. The reaction was maintained for 4 h at 65°C and atmospheric pressure. After reaction, the mixture was rotary evaporated at 45°C to remove the excess methanol, while the products, unreacted triacetin and the solid catalyst were left in the reactor. Then the catalyst was separated by centrifuging, washed with water and calcinated at 100°C for reuse. The liquid mixture was measured by GC. In addition, we have checked the mixture before and after rotary evaporator by GC which confirmed that there was no additional reaction because the time (1 min) was too short to allow any additional reactions occur.

### Results and Discussion

#### Structural characterization of the catalysts.

The elemental analyses of HPW$_{11}$M were given in Table 1. These results confirmed the molar ratio of P: W: M = 1:11:1, which showed the formation of mono-metal substituted undeca-tungstophosphates.

Four bands were shown at 1072($\nu_{as}$ P-O), 977 ($\nu_{as}$ W-O-W), 891 ($\nu_{as}$ W-O-W intra-octahedral), and 796 cm$^{-1}$ ($\nu_{as}$ W-O-W inter-octahedral) in the FTIR spectra of HPW$_{11}$M (Fig. 1A), which were attributed to the stretching vibrational peaks of HPA Keggin anions$^{22}$. Compared with PW$_{11}$O$_{40}$$^{7-}$ (1082, 957, 873, and 763 cm$^{-1}$), some shifts ($\nu_{as}$ W-O and $\nu_{as}$ W-O-W) occurred due to the substitution of W by M ions to form saturated HPAs (Scheme S1). The FTIR spectra of HPW$_{11}$M were similar to that of H$_3$PW$_{12}$O$_{40}$ (1080, 982, 890, and 797 cm$^{-1}$), which showed the replacement of tungsten by metal cations formed a dodecatungstophosphoric Keggin structure successfully. The IR spectrum gave a band at 580 cm$^{-1}$ which indicated the existence of an M-O bond$^{23}$. The FTIR spectra of HPW$_{11}$M and PW$_{11}$O$_{40}$$^{7-}$ clusters and the formation of good crystals with the Keggin structure.

The morphology of H$_3$PW$_{11}$Ti was measured by SEM and EDAX (Fig. S1). It showed that as-prepared material displayed well-shaped crystalline particles with molar ratio of W: P: Ti = 11.07: 1.14: 1.13.

#### The acidic properties of the catalysts.

The FT-IR spectra of pyridine absorption are a powerful tool for identifying the nature of acid sites$^{21}$. As shown in Fig. 2, HPW$_{11}$M presented typical bands at 1489 cm$^{-1}$ which confirmed that there was no additional reaction because the time (1 min) was too short to allow any additional reactions occur. The conversion of glycerol and selectivity of glycerides were calculated by the following equations:

$$
Conversion(\%) = \frac{\text{moles of glycerol (in)} - \text{moles of glycerol (out)}}{\text{moles of glycerol (in)}} \times 100\%
$$

$$
Selectivity(\%) = \frac{\text{moles of one product}}{\text{moles of all products}} \times 100\%
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$$

$$
Selectivity(\%) = \frac{\text{moles of one product}}{\text{moles of all products}} \times 100\%
$$
The total contents of Brønsted acid and Lewis acid were obtained from titration with n-butylamine and the separated density was calculated from the strength ratio of Brønsted acid and Lewis acid in FT-IR spectra of pyridine absorption (Table 1). It was found that mono-substituted HPW\(_{11}\) gave decreasing trend compared with their parent H\(_3\)PW\(_{12}\)O\(_{40}\) for single Brønsted acid content. In addition, different catalysts showed different Lewis acid and Brønsted acid contents.

### Table 1. The characterization of H\(_n\)PW\(_{11}\)M.

| Catalyst          | Elemental results (calculated values in parenthesis)/wt% | \(^a\)Brønsted acidity (mmol/g) | \(^b\)Lewis acidity (mmol/g) | \(^c\)Total acidity (mmol/g) |
|-------------------|----------------------------------------------------------|---------------------------------|------------------------------|------------------------------|
|                   | H | P | W | M          |                            |                                |                             |                             |
| H\(_3\)PW\(_{12}\)O\(_{40}\) | 1.75 | 0.03 | 1.78 | 1.86 | \(^a\) | \(^b\) | \(^c\) |
| Ti\(_{0.25}\)H\(_2\)PW\(_{12}\)O\(_{40}\) | 0.12(0.09) | 1.22(1.38) | 96.73(98.00) | 0.44(0.53) | 1.94 | 0.65 | 2.59 | 2.67 |
| H\(_5\)PW\(_{11}\)TiO\(_4\) | 0.18(0.18) | 1.13(1.13) | 74.04(73.64) | 1.71(1.74) | 1.59 | 0.56 | 2.15 | 2.20 |
| H\(_5\)PW\(_{11}\)CuO\(_3\) | 0.18(0.18) | 1.23(1.13) | 73.61(73.65) | 2.44(2.31) | 1.52 | 0.41 | 1.93 | 1.98 |
| H\(_5\)PW\(_{11}\)SnO\(_3\) | 0.17(0.11) | 1.14(1.11) | 73.84(72.25) | 3.99(4.24) | 1.22 | 0.32 | 1.54 | 1.61 |
| H\(_5\)PW\(_{11}\)ZrO\(_4\) | 0.18(0.18) | 1.13(1.11) | 72.53(72.5) | 3.34(3.27) | 1.14 | 0.25 | 1.39 | 1.45 |
| H\(_5\)PW\(_{11}\)ZnO\(_3\) | 0.17(0.18) | 1.32(1.13) | 73.53(73.60) | 2.01(2.38) | 1.12 | 0.21 | 1.33 | 1.42 |
| H\(_4\)PW\(_{11}\)AlO\(_3\) | 0.15(0.15) | 1.11(1.14) | 74.11(74.23) | 1.04(0.99) | 0.59 | 0.60 | 1.19 | 1.21 |
| H\(_4\)PW\(_{11}\)FeO\(_3\) | 0.14(0.15) | 1.10(1.13) | 73.04(73.88) | 1.89(2.04) | 0.57 | 0.58 | 1.15 | 1.19 |
| H\(_4\)PW\(_{11}\)CrO\(_3\) | 0.14(0.15) | 1.11(1.13) | 72.82(73.99) | 1.94(1.90) | 0.54 | 0.40 | 0.94 | 0.98 |

This figure is to confirm the Keggin structure of H\(_n\)PW\(_{11}\)MO\(_3\) catalysts.

**Figure 1.** FTIR spectra (A) and XRD patterns (B) of H\(_n\)PW\(_{11}\)MO\(_3\) catalysts. This figure is to confirm the Keggin structure of H\(_n\)PW\(_{11}\)MO\(_3\) catalysts.

**Figure 2.** FTIR spectra of pyridine adsorption of H\(_n\)PW\(_{11}\)MO\(_3\) catalysts. This figure is a powerful tool for identifying the nature of acid sites, especially to distinguish the Lewis acid and Brønsted acid.

The total contents of Brønsted acid and Lewis acid were obtained from titration with n-butylamine and the separated density was calculated from the strength ratio of Brønsted acid and Lewis acid in FT-IR spectra of pyridine absorption (Table 1). It was found that mono-substituted HPW\(_{11}\) gave decreasing trend compared with their parent H\(_3\)PW\(_{12}\)O\(_{40}\) for single Brønsted acid content. In addition, different catalysts showed different Lewis acid and Brønsted acid contents.
Lewis metals gave the HPAs with different proton numbers, i.e. the proton numbers were four for Al, Fe and Cr, five for Ti, Cu, Zn and Zr, three for Sn, respectively. For H3PW12O40, the length of M-O bond decreased as the order of Z/r which is Ti4+ (7.55) > Zr3+ (5.55) > Zn2+ (3.33) > Cu2+ (3.23). The oxygen attraction of different metals increased in the same order, which might lead to the decrease of proton attraction. Therefore, protons could easily dissociate from HPAs for H5PW11TiO40 and give low value of dissociation constants (the pK1). For H3PW12O40 (Al, Fe, and Cr), the Z/r values were 7.69, 6.12, and 4.84, respectively, which decided the Bronsted acidity in the following sequence: H5PW11AlO40 > H5PW11TiO40 > H5PW11FeO40. Therefore, the metals with higher Lewis acidity such as Ti and Al could give higher Bronsted acidity. Timofeeva15 demonstrated some dissociation constants (the pK1) in AcOH as \( \text{H}_5 \text{PW}_{11} \text{TiO}_{40} \rightarrow \text{H}_5 \text{PW}_{11} \text{TiO}_{39} + \text{H}^+ \) and 1 h. Extending the reaction time could enhance the selectivities to DAG and TAG (Fig. 3a). We have reported a series of TiHx3PW12O40 with higher acidity which was prepared by exchanging the protons of H3PW12O40 with different numbers of Ti4+ ions (Scheme S1). The difference of Bronsted acidity between H5PW11TiO40 and H3PW12O40 was attributed to the different negative charges of anions, which was −5 for H5PW11TiO40 and −3 for Ti25H2PW12O40, respectively. Because of the larger number of negative charges, the protons dissociation of H5PW11TiO40 was more difficult compared with Ti25H2PW12O40. The order of acidic capacity for Ti1-H3PW12O40 was Ti10H2PW12O40 > Ti13H3PW12O40 > Ti15H4PW12O40 > Ti17H5PW12O40 > Ti19H6PW12O40 > Ti21H7PW12O40 with 2.886 mol·kg\(^{-1}\)) > Ti13H3PW12O40 (2.705 mol·kg\(^{-1}\)) > Ti15H4PW12O40 (2.671 mol·kg\(^{-1}\)) > Ti17H5PW12O40 (2.663 mol·kg\(^{-1}\)) > Ti19H6PW12O40 (2.614 mol·kg\(^{-1}\)) > Ti21H7PW12O40 (2.496 mol·kg\(^{-1}\)) > Ti23H8PW12O40 (2.469 mol·kg\(^{-1}\)). For Ti25H2PW12O40 series, the strength of acidic property was not incoherent with the number of protons, but was influenced significantly by the number of metals. Ti25H2PW12O40 gave a higher Bronsted acidity than H5PW11TiO40, which might be attributed to that Ti shared the attraction force from PW12O40 with proton. In this case, proton could easily dissociate from polyoxoanions which would give a higher dissociation constant than H5PW11TiO40. Therefore, the combination of Ti and H resulted in the higher Bronsted acidity.

**Catalytic activity of HPWM catalysts in esterification.** Commonly, Bronsted acid is active mainly in esterification, whereas Lewis acid is more active in transesterification26. However, some research showed that Lewis acid is also active in esterification of glycerol. Zhu's group recently reported a highly-active silver-exchanged phosphotungstic acid catalyst Ag1H2PW12O40 which was applied in glycerol esterification with acetic acid, with 96.8% conversion and 48.4, 46.4 and 5.2% selectivity to MAG, DAG and TAG, respectively, and the reaction conditions were 120 °C, 15 min with the molar ratio of 10:1. The high efficiency came from the contribution of Lewis metal Ag1+. N. Lingaiah's group also reported the esterification of glycerol with acetic acid, with 96.8% conversion and 48.4, 46.4 and 5.2% selectivity to MAG, DAG and TAG, respectively, and the reaction conditions were 120 °C, 15 min with the molar ratio of 10:1. Extending the reaction time could enhance the selectivities to DAG and TAG (Fig. 3a). It was found that from 0.25 h to 4 h, the selectivity toward MAG obviously decreased to 3.3% while the total selectivity to DAG and TAG increased to 96.7%. For H5PW11ZrO40 and H5PW11ZnO40 with almost the same Lewis acidity, but the former tended to produce more DAG while the later was fond of MAG,

\[ \text{HOAc} + \text{H}_3 \text{PW}_11 \text{M} \rightarrow \text{H}_5 \text{PW}_11 \text{M} \rightarrow \text{MAG} + \text{H}_2 \text{O} \]
respectively. From the point of ionic radii for the two ions, the steric crowding around Lewis acid centers decreased with the increase of ionic radii from Zn$^{2+}$ (0.60 Å) to Zr$^{4+}$ (0.72 Å); therefore, in the same reaction conditions, H$_5$PW$_{11}$ZrO$_{40}$ gave more yield of DAG than H$_5$PW$_{11}$ZnO$_{39}$.

For H$_5$PW$_{11}$TiO$_{40}$ and Ti$_{0.25}$H$_2$PW$_{12}$O$_{40}$, the turnover frequencies (TOFs = conversion of glycerol/amount of catalyst (mmol) × time) were 1007.86 and 1055.10 mmol/mmol·h, respectively. The conversion of glycerol was followed the equation obtained by Kozhevnikov et al.\textsuperscript{27}: \( \log k = 1.04H_0 - 3.46 \), where \( k \) is expressed as the rate constant, and \( H_0 \) is the acidity function of the catalyst solution. Therefore, the catalytic activity of Ti$_{0.25}$H$_2$PW$_{12}$O$_{40}$ was higher than that of H$_5$PW$_{11}$TiO$_{40}$, which meant that higher Brønsted acidity gave higher glycerol conversion. This was also suitable for the other HPAs substituted by metals.

The different selectivities to different esters might be attributed to the pore size distributions of these two catalysts (The pore sizes were 5.62 and 3.83 nm corresponding to H$_5$PW$_{11}$TiO$_{40}$ and Ti$_{0.25}$H$_2$PW$_{12}$O$_{40}$, respectively). The large size of H$_5$PW$_{11}$TiO$_{40}$ permitted higher selectivities to DAG and TAG.

From the above equations, we could know that water was by-product of the glycerol esterification reaction. Hence, the solid acid catalyst was easily destroyed by water in the system. So a water-tolerant solid acid catalyst was desirable. When adding extra water to the reaction system, catalytic activity of the two catalysts could be influenced (Fig. 4). In view of H$_4$PW$_{11}$AlO$_{39}$, the water content ranging from 0 to 0.6 wt% did not play a significant role in the glycerol conversion, which meant that H$_4$PW$_{11}$AlO$_{39}$ catalyst exhibited a certain water-tolerant property. On the contrary, the catalytic activity of H$_5$PW$_{12}$O$_{40}$ decreased dramatically as the growth of water from 0.1 to 0.6 wt%, which suggested that H$_3$PW$_{12}$O$_{40}$

| Catalysts      | CON(%) | MAG(%) | DAG(%) | TAG(%) | Total selectivity to DAG and TAG | TOF$^b$ (mmol/mmol·h) |
|----------------|--------|--------|--------|--------|----------------------------------|----------------------|
| H$_5$PW$_{11}$TiO$_{40}$ | 97.4   | 37.9   | 55.4   | 6.7    | 62.1                             | 1007.86              |
| Ti$_{0.25}$H$_2$PW$_{12}$O$_{40}$ | 95.0   | 52.5   | 39.6   | 7.9    | 47.5                             | 1055.10              |
| H$_5$PW$_{11}$CuO$_{39}$   | 94.9   | 54.0   | 43.6   | 2.4    | 46.0                             | 981.88               |
| H$_5$PW$_{11}$SnO$_{39}$   | 77.9   | 76.1   | 22.9   | 1.0    | 23.9                             | 821.61               |
| H$_5$PW$_{11}$ZrO$_{40}$   | 75.3   | 54.4   | 34.3   | 11.4   | 45.8                             | 791.49               |
| H$_5$PW$_{11}$ZnO$_{39}$   | 73.5   | 89.8   | 9.0    | 1.2    | 10.2                             | 760.97               |
| H$_5$PW$_{11}$AlO$_{39}$   | 71.9   | 88.5   | 11.2   | 0.3    | 11.5                             | 733.73               |
| H$_5$PW$_{11}$FeO$_{39}$   | 70.6   | 84.1   | 15.4   | 0.5    | 15.9                             | 728.15               |
| H$_5$PW$_{11}$CrO$_{39}$   | 66.9   | 74.8   | 24.4   | 0.8    | 32.4                             | 689.00               |

Table 2. The comparison between different catalysts on esterification reaction\textsuperscript{a}.  
\textsuperscript{a}Reaction conditions: Molar ratio of glycerol to acetic acid = 1:5, 75 °C, 3 wt% of catalyst, and 60 min.  
\textsuperscript{b}TOF = n(Gly) × conversion/time·n(catalyst)\textsuperscript{c}.

![Figure 3. Glycerol conversion and selectivity as a function of reaction time over H$_5$PW$_{11}$TiO$_{40}$ and H$_5$PW$_{12}$O$_{40}$. Reaction conditions: 75 °C, glycerol/acetic acid = 1:5 (molar ratio), 3 wt% catalyst loading relative to glycerol. This figure is to confirm that extending the reaction time could enhance the selectivities to DAG and TAG which are our target products.](image-url)
was not water-tolerant. It was reported that if H₂O molecules were added, they would link with O–H to form O–H····H₂O. In the IR spectra of HPAs adsorbing H₂O (Fig. S2), the peak at 1670 cm⁻¹ (corresponding to hydrated OH stretching vibrational peak) belonging to H₅PW₁₁TiO₄₀ was bigger than that of H₃PW₁₂O₄₀, which indicated that more water molecules could be adsorbed by H₅PW₁₁TiO₄₀ than by H₃PW₁₂O₄₀. Therefore, the water-tolerance of H₅PW₁₁TiO₄₀ was better than that of H₃PW₁₂O₄₀. But further increasing the amount of water, the ability of water-tolerance could be destroyed. The different water-tolerance determined that H₃PW₁₂O₄₀ could not give the selectivities to DAG and TAG as high as H₅PW₁₁TiO₄₀.

Catalytic activity of HPW₁₁M catalysts in transesterification. Based on the suggestion by Santacesaria, Brønsted acid catalysts were active mainly in esterification while Lewis acid catalysts were more active in transesterification. In order to evaluate the efficiency of the HPW₁₁M on transesterification, glycerol triacetin was selected to investigate the influence of their Lewis and Brønsted acidity (Table 3). It is known that triglyceride transesterification with methanol is a consecutive reaction including three continuous steps:  

\[
\text{glycerol triacetin} \rightarrow \text{glycerol triolein} + \text{acetoin} \rightarrow \text{glycerol triolein} + \text{acetone} \rightarrow \text{glycerol} + \text{acetone} + \text{acetic acid}
\]

Figure 4. The water-tolerant tests for H₅PW₁₁TiO₄₀ and H₃PW₁₂O₄₀. Reaction conditions: 75 °C, glycerol/acetic acid = 1: 5 (molar ratio), 3 wt% catalyst loading relative to glycerol, 20 min. This figure is to confirm that when adding extra water to the reaction system, catalytic activity of the two catalysts could be influenced. which meant that H₅PW₁₁TiO₄₀ catalyst exhibited a certain water-tolerant property. While H₃PW₁₂O₄₀ was not water-tolerant.

| catalyst          | CON(%) | GLY(%) | MAG(%) | DAG(%) | TOFb (mmol/mmol·h) |
|------------------|--------|--------|--------|--------|-------------------|
| Ti₀.25H₂PW₁₂     | 99.8   | 89.1   | 10.7   | 0.2    | 70.69             |
| H₃PW₁₂O₄₀       | 99.2   | 89.5   | 10.1   | 0.4    | 70.00             |
| H₅PW₁₁TiO₄₀     | 92.2   | 83.3   | 12.2   | 4.5    | 62.03             |
| H₅PW₁₁CuO₃₉     | 82.3   | 59.8   | 26.1   | 14.1   | 55.36             |
| H₅PW₁₁SnO₃₉     | 69.3   | 4.3    | 43.4   | 52.3   | 47.83             |
| H₅PW₁₁ZrO₄₀     | 65.8   | 8.5    | 17.5   | 74.0   | 44.97             |
| H₅PW₁₁ZnO₃₉     | 64.3   | 20.7   | 34.6   | 44.7   | 43.29             |
| H₅PW₁₁AlO₃₉     | 44.4   | 32.5   | 2.6    | 64.9   | 29.63             |
| H₅PW₁₁FeO₃₉     | 36.6   | 41.7   | 31.5   | 26.8   | 24.54             |
| H₅PW₁₁CrO₃₉     | 20.4   | 58.2   | 37.6   | 4.2    | 13.66             |

Table 3. The comparison between different catalysts on transesterification.  

aReaction conditions: molar ratio of TAG to methanol = 1:6, 65 °C, 4 wt% of catalyst, and 4h. bTOF = n(TAG) × conversion/time·n(catalyst).
Table 3 showed that conversion of glycerol triacetin changed in the order of Ti0.25H2PW12O40 > H3PW12O40 > H5PW11CuO39 > H5PW11SnO39 > H5PW11ZrO40 > H5PW11ZnO39 > H5PW11AlO40 > H5PW11FeO39 > H4PW11CrO39. For TOF, the order was as following: Ti0.25H2PW12O40 > H3PW12O40 > H5PW11CuO39 > H5PW11SnO39 > H5PW11ZrO40 > H5PW11ZnO39 > H5PW11AlO40 > H5PW11FeO39 > H4PW11CrO39. The results suggested that HPA catalysts with higher acidity were in favor of high TOF for transesterification of triacetin. The selectivity to glycerol was in the range of Ti0.25H2PW12O40 > H3PW12O40 > H5PW11CuO39 > H5PW11SnO39 > H5PW11ZrO40 > H5PW11ZnO39 > H5PW11AlO40 > H5PW11FeO39 > H4PW11CrO39. HPAs with higher Lewis acidity such as Cr, Fe gave higher selectivity to glycerol and tended to promot the conversion of diacetin and monoacetin to glycerol and methyl acetate.

Main parameters of the transesterification reaction catalyzed by H5PW11TiO40 including temperature, reaction time, catalyst dosage and molar ratio of TAG to methanol were investigated (Fig. S4). In order to obtain high yield of glycerol, high molar ratio of triacetin to methanol (1:6), long reaction time (4 h), and 65 °C were needed, with which we have got a 92.2% conversion and a 83.3% selectivity of glycerol, respectively.

It might be more important to convert low quality feedstocks to biodiesel. However, the presence of high FFAs might have adverse effects on the catalyst activity. H5PW11TiO40 might catalyze the esterification of FFA and transesterification of triacetin simultaneously. Therefore, the conversion of triacetin with some FFA contents was catalyzed by H5PW11TiO40 with Lewis acidity and Brønsted one (Fig. S5).

Reuse of catalysts. It is necessary to determine the nature of H5PW11TiO40 in esterification or transesterification. The solubility of H5PW11TiO40 in acetic acid and methanol was measured by Uv-Vis spectroscopy (Fig. S6). We could see that H5PW11TiO40 was insoluble either in acetic acid or in methanol, which suggested that it performed as a heterogeneous catalyst in both esterification and transesterification reactions. The behavior was attributed to the calcinations treatment to H5PW11TiO40 at 200 °C for about 3 h to form insoluble powders which were also determined by the SEM image and EDAX (Fig. S1). In other word, the catalyst could be easily separated from the production mixture. The catalyst was separated by centrifuging and decanted from the bottom of the reactor, and then washed with ethanol and dried at 60 °C overnight for further reaction cycles. As shown in Fig. 5, there was no considerable change in the catalytic activity after five reaction cycles either in esterification or transesterification. The
IR spectrum of the products in transesterification (Fig. S7) indicate that no characteristic peaks corresponding to $H_5PW_{11}TiO_{40}$ were observed in range of 790 to 1000 cm$^{-1}$, which demonstrated that the leaching of $H_5PW_{11}TiO_{40}$ was negligible. The leaching of $H_5PW_{11}TiO_{40}$ was about 0.10 wt% and 0.12 wt% during esterification and transesterification for one cycle, respectively. To further determine the leaching of $H_5PW_{11}TiO_{40}$, the catalyst was separated after reacting for 20 min (91.0% of glycerol conversion) and was allowed to react further for over 1 h at the same conditions. The result showed that the conversion of glycerol was only 92.4%, which meant that $H_5PW_{11}TiO_{40}$ acted as a heterogeneous catalyst.

The stability of HPAs during the reaction was determined by IR spectroscopy (Fig. S8). After the reaction, the catalysts still kept its Keggin structure. The peaks at 1072, 977, 891, and 796 cm$^{-1}$ attributing to the characteristic bands of Keggin structure could also be observed. The SEM image of the catalyst after reaction (Fig. S9) showed no-change of the morphology during the reaction. Therefore, HPAs was stable and could be reused at least for five cycles.

**Conclusion**

This work demonstrated a variety of HPAs $H_nPW_6M$ ($M = Ti^{IV}$, Cu$^{II}$, Al$^{III}$, Sn$^{IV}$, Fe$^{III}$, Cr$^{III}$, Zr$^{IV}$ and Zn$^{II}$) with both Lewis and Brønsted acidity. The influence of these Lewis metals on the acidic strength of dodecatungstates showed that (1) moderated Lewis metals gave more influence on total acidity including Ti and Cu; (2) compared to Ti,H$_{14}$P$_{2}W_{12}O_{40}$ Ti in substituted place played a less important role on total acidity. Their catalytic activities in esterification of glycerol and transesterification of triglycerides were generally followed their acidic properties. Among all these HPAs, $H_5PW_{11}TiO_{40}$ displayed properties like Lewis acid sites, insolubility in polar solvents, water-tolerance, acid-tolerance, and stability which were benefit to its excellent performance. To the best of our knowledge, $H_5PW_{11}TiO_{40}$ gave the highest selectivity to desired DGA and TGA (96.7%) in the esterification of glycerol which was higher than the reported Ag,$H_5PW_{11}O_{40}$. Moreover, in transterification, high conversion of triacetin and high yield of glycerol were obtained by $H_5PW_{11}TiO_{40}$. Furthermore, $H_5PW_{11}TiO_{40}$ did not suffer from leaching and deactivation in five reaction cycles either in esterification or transesterification reactions.

This study provides useful information on Lewis metal substituted HPAs. It could be a promising candidate for the catalytic esterification of glycerol and synthesis of valuable biofuel additives, meanwhile, it could also act as a potential catalyst for production of biodiesel using low quality feedstocks.

**References**

1. Okuhara, T. Water-tolerant solid acid catalysts. *Chem Rev* **102**, 3641–3665 (2002).
2. Koizushima, I. V. Catalysis by heteropoly acids and multicomponent polyoxometalates in liquid-phase reactions. *Chem Rev* **98**, 171–198 (1998).
3. Kaur, J. & Koizushima, I. V. Efficient acylation of toluene and anisole with aliphatic carboxylic acids catalysed by heteropoly salt Cs$_2$H$_2$P$_2$WO$_{12}$. *Chem Commun* **21**, 2508–2509 (2002).
4. Baba, T. et al. Generation of acidic sites in metal salts of heteropoly acids. *J Phys Chem B* **87**, 2406–2411 (1983).
5. Boglio, C. et al. Increased Lewis acidity in hafnium-substituted polyoxometalates. *Chem Eur J* **13**, 5426–5432 (2007).
6. Kikukawa, Y. et al. Synthesis and catalysis of di- and tetraneuclear metal sandwich-type silicotungstates [(gamma-SiW$_{10}$O$_{36}$)$_2$M$_2$(mu$_4$-O)(mu-OH)$_6$] and [(gamma-SiW$_{10}$O$_{36}$)$_2$M$_4$(mu$_4$-O)(mu-OH)$_8$] (M = Zr or Hf). *J Am Chem Soc* **130**, 5472–5478 (2008).
7. Yamamoto, H. From designer Lewis acid to designer Brønsted acid towards more reactive and selective acid catalysis. *Proc Jpn Acad Ser B* **84**, 134–146 (2008).
8. Shimizu, K. et al. Effects of Bronsted and Lewis acidities on activity and selectivity of heteropolyacid-based catalysts for hydrolysis of cellobiose and cellulose. *Green Chem* **11**, 1627–1632 (2009).
9. Chambon, F. et al. Cellulose hydrothermal conversion promoted by heterogeneous Bronsted and Lewis acids: Remarkable efficiency of solid Lewis acids to produce lactic acid. *Appl Catal B: Environ* **105**, 171–181 (2011).
10. Suzuki, K. et al. Strategic design and refinement of Lewis acid-base catalysis by rare-earth-metal-containing polyoxometalates. *Inorg Chem* **51**, 6953–6961 (2012).
11. Shi, W. et al. Effects of Bronsted and Lewis acidities on catalytic activity of heteropolyacids in transesterification and esterification reactions. *Chem Eng Technol* **35**, 347–352 (2012).
12. Zhao, Q. et al. Acid-base bifunctional HPA nanocatalysts promoting heterogeneous transesterification and esterification reactions. *Catal Sci Technol* **3**, 2204–2209 (2013).
13. Shimizu, K. et al. Polyvalent-metal salts of heteropolyacid as catalyst for Friedel-Crafts alkylation reactions. *Appl Catal A* **349**, 1–5 (2008).
14. Zhu, S. H. et al. Design of a highly active silver-exchanged phosphotungstic acid catalytic for glycerol esterification with acetic acid. *J Catal* **306**, 155–163 (2013).
15. Jagadeeswaraha, K. et al. Incorporation of Zn$^{II}$ ions into the secondary structure of heteropoly tungstate: catalytic efficiency for synthesis of glycerol carbonate from glycerol and urea. *Catal Sci Technol* **4**, 2969–2977 (2014).
16. Timofeeva, M. N. Acid catalysis by heteropoly acids. *Appl Catal A: Gen* **256**, 19–35 (2003).
17. Brevard, C. et al. Tungsten-183 NMR: a complete and unequivocal assessment of the tungsten-tungsten connectivities in heteropolytungstates via two-dimensional183 W NMR techniques. *J Am Chem Soc* **105**, 7059–7063 (1983).
18. Goncalves, C. E. et al. Biosaditive synthesis from H$_3PW_4O$_{12}-catalyzed glycerol esterification with HOAc under mild reaction conditions. *Fuel Process Technol* **102**, 46–52 (2012).
19. Tronchea, S. B. et al. Hydroxylated magnesium fluorides as environmentally friendly catalysts for glycerol acetylation. *Appl Catal B: Environ* **107**, 260–267 (2011).
20. Pizzio, L. R. & Blanco, M. N. A contribution to the physicochemical characterization of nonstoichiometric salts of tungstosilicic acid. *Microporous Mesoporous Mater* **103**, 40–47 (2007).
21. Emeis, C. A. Determination of integrated molar extinction coefficients for infrared absorption bands of pyridine adsorbed on solid acid catalysts. *J Catal* **141**, 347–354 (1993).
22. Igen, F. et al. Conversion of carbohydrates into 5-hydroxymethylfurfural in highly concentrated low melting mixtures. *Green Chem* **11**, 1948–1954 (2009).
23. Zhao, J. et al. A Brønsted-Lewis-surfactant-combined heteropolyacid as an environmental benign catalyst for esterification reaction. Catal Commun. 20, 103–106 (2012).
24. Kourieh, R. et al. Investigation of the WO₃/ZrO₂ surface acidic properties for the aqueous hydrolysis of cellulose. Catal Commun. 19, 119–126 (2012).
25. Budarin, V. L. et al. Tunable mesoporous optimised for aqueous phase esterifications. Green Chem. 9, 992–995 (2007).
26. Penzien, J. et al. Heterogeneous catalysts for hydroamination reactions: structure-activity relationship. J Catal 221, 302–312 (2004).
27. Kozhevnikov, I. V. et al. Mechanism of isobutylene hydration in aqueous solution in the presence of heteropoly acid. Kinet Katal 30, 50–54 (1989).
28. Peze, C. et al. H₂O interaction with solid H₃PW₁₂O₄₀: An IR Study. Langmuir. 16, 8139–8144 (2000).
29. Misono, M. Unique acid catalysis of heteropolycompounds (heteropolyoxometalates) in the solid state. Chem Commun. 13, 1141–1152 (2001).
30. Di Serio, M. et al. Synthesis of biodiesel via homogeneous Lewis acid catalyst. J Mol Catal A: Chem 239, 111–115 (2005).
31. Lopez, D. E. et al. Transesterification of triacetin with methanol on solid acid and base catalysts. Appl Catal A: Gen. 295, 97–105 (2005).

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Author Contributions
M.T. conducted most experiments with help from L.X. Z.S. provided assistance in imaging and data analysis. S.W., X.Wang. and J.S. provided scientific guidance. M.T. wrote the manuscript with help from X.W. All authors reviewed the manuscript.

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