Elsevier Editorial System(tm) for Fuel
Manuscript Draft

Manuscript Number:

Title: Amino acid-functionalized heteropolyacids as efficient and recyclable catalysts for esterification of palmitic acid to biodiesel

Article Type: Original Research Paper

Keywords: Polyoxometalate; Heteropolyacid; Biodiesel; Reaction engineering

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Abstract: The organic-inorganic hybrid catalysts, namely [GlyH]xH3-xPW12O40 (x = 1.03.0), prepared by mixing varied amounts of glycine (Gly) and tungstophosphoric acid (TPA) were characterized by different analytical and spectroscopic techniques such as TGA, XRD, FT-IR, and 1H and 13C NMR. In particular, their acidic properties were probed by solid-state 31P MAS NMR of adsorbed trimethylphosphine oxide. The catalytic performances of various Gly-TPA catalysts during esterification reaction of palmitic acid with methanol for production of methyl palmitate were illustrated and examined. The catalyst system revealed self-separation characteristics, forming biphasic product/catalyst layers to render facile product separation and catalyst recycling. The [GlyH]1.0H2.0PW12O40 catalyst was found to exhibit the best activity with an optimal biodiesel yield of 93.3%.

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Cover Letter

Dear Editors:

It gives me pleasure to submit this paper to Fuel as an original paper.

In this work, we report on the preparation of a series of amino acid-functionalized heteropolyacids catalysts and their application in biomass conversion, in particular, for the synthesis of methyl palmitate (biodiesel). Owing to the advantages of easy degradation, non-toxic, low sulfur content, and environmentally benign, biodiesel has gained substantial attention and has becoming an alternative feedstock to replace fossil fuels. Conventionally, the production of FAME mostly invokes homogeneous catalysis over acidic catalysts such as H_2SO_4, HCl, H_3PO_4 or organic sulfuric acids, which are also handicapped by formidable recovery and recycling. The organic-inorganic hybrid catalysts reported herein not only possess ultra-high acidity favorable for high ester yield (> 90%) but also superior durability. More importantly, the catalytic reaction invokes a homogeneous reaction process, which was made possible by the "self-separation" characteristics of these peculiar catalysts, thus, rendering facile product separation and catalyst recycling.

It is declared that this work has not been published previously and not under consideration for publication elsewhere. We believe that this paper should provide new and important insights to the understanding of novel environmental benign catalysts and relevant applications in clean synthesis, hence, should draw some interests to the broad readership of Fuel.

Your kind editorial assistance and efforts in making a thorough review of this paper are gratefully acknowledged.

Best regards.

Yours Sincerely,

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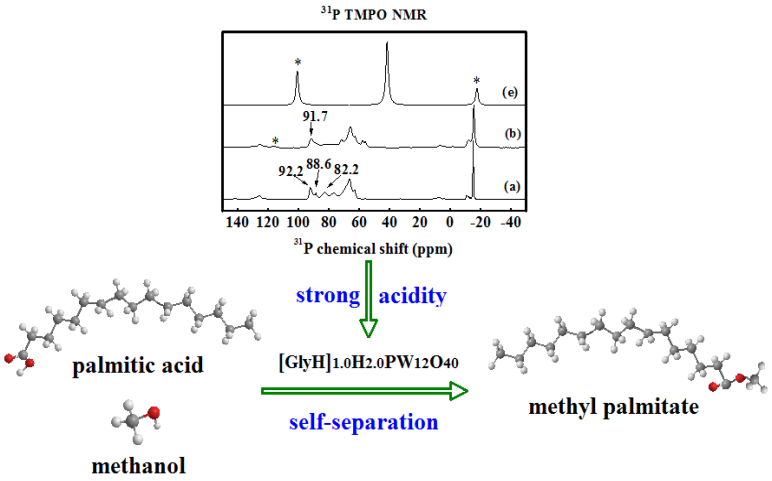
Research Highlights

- Amino acid-grafted heteropolyacids show high activity for conversion of fatty acid.
- Organic salt catalysts show strong acidity desirable for esterification reaction.
- Catalyst system shows self-separation property favorable for separation/recycling.
- Acidic properties probed of catalysts probed by ^{31}P NMR of trimethylphosphine oxide.

Graphical abstract

Amino acid-functionalized heteropolyacid catalysts show superior activity, durability, and unique self-separation property desirable for facile recovery and recycling for conversion of free fatty acids to biodiesel.



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Amino acid-functionalized heteropolyacids as efficient and recyclable catalysts for esterification of palmitic acid to biodiesel

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ABSTRACT

The organic-inorganic hybrid catalysts, namely $[GlyH]_xH_{3-x}PW_{12}O_{40}$ (x = 1.0–3.0), prepared by mixing varied amounts of glycine (Gly) and tungstophosphoric acid (TPA) were characterized by different analytical and spectroscopic techniques such as TGA, XRD, FT-IR, and ^{1}H and ^{13}C NMR. In particular, their acidic properties were probed by solid-state ^{31}P MAS NMR of adsorbed trimethylphosphine oxide. The catalytic performances of various Gly-TPA catalysts during esterification reaction of palmitic acid with methanol for production of methyl palmitate were illustrated and examined. The catalyst system revealed self-separation characteristics, forming biphasic product/catalyst layers to render facile product separation and catalyst recycling. The $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ catalyst was found to exhibit the best activity with an optimal biodiesel yield of 93.3%.

Keywords: Polyoxometalate; Heteropolyacid; Biodiesel; Reaction engineering

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1. Introduction

Biodiesel represents renewable diesel fuel consists of long-chain alkyl esters such as fatty acid methyl esters (FAME) normally derived by transesterification of fats (e.g., vegetable oils or tallow) with methanol [1]. Owing to the advantages of easy degradation, nontoxic, low sulfur content, and environmentally benign, biodiesel has gained substantial attention and has becoming an alternative feedstock to replace fossil fuels [2]. Conventionally, the production of FAME mostly invokes homogeneous catalysis over acidic catalysts such as H_2SO_4, HCl, H_3PO_4 or organic sulfuric acids [3]. However, these mineral acids are hampered by several inherent drawbacks, such as corrosion and toxicity, which together militate against their applications for continuous processing, particularly during neutralization and separation steps. Thus, considerable R&D efforts have been made on the development of heterogeneous catalyst systems for esterification of free fatty acids (FFAs) to biodiesel. For examples, solid acid catalysts such as metal oxides [4,5], zeolites [6,7], heteropolyacids (HPAs) [8,9] and so on, have been exploited for biodiesel production, rendering facile waste management, products separation as well as catalyst recycling as compared to the conventional homogeneous systems [10].

Heteropolyacids, which possess ultra-strong Brønsted acidity and unique pseudo-liquid properties, exhibit excellent oxidizing capability and have been widely used as homogeneous and heterogeneous catalysts [11]. HPAs are also appreciated as environmentally benign catalysts due to their stable and relatively nontoxic characteristics. To circumvent their low surface area nature, the protic HPAs are frequently immobilized on porous supports to facilitate high catalytic activity as well as facile products separation and catalyst recycling. However, the main feature that compromise the extensive utilization of supported HPAs catalysts is their high solubility in polar

solvents, which in turn leads to severe leaching of HPA from the solid supports. An alternative approach is *via* exchanging Brønsted protons (H^+) of HPAs with various metal ions, e.g., Cu^{2+} [12], Ag^+ [13], or K^+ [14] to form insoluble salts. Comparing to their homogeneous counterparts, such solid acid catalysts are anticipated to have superior stability, nonetheless, the nanocrystalline size of the tertiary structure of HPA remains as a critical limitation for separation and reuse [11]. Consequently, considerable recent research interests have been focusing on the development of novel organic-inorganic composites of HPA-base ionic liquid (IL) catalysts and their applications for esterification reactions and conversions of biomass [15–17].

Herein, we report the synthesis of a series of organic-inorganic composite catalysts by using amino acid and HPA as precursors. More specifically, the amino acid-functionalized HPA catalysts were prepared by combining glycine (NH_2CH_2COOH; Gly), the smallest amino acid commonly found in proteins, with tungstophosphoric acid ($H_3PW_{12}O_{40}$; TPA), one of the most typical HPAs with Keggin-type structure, as the organic and inorganic ingredient, respectively, under different composition ratios. The resultant low-cost, nontoxic, and water soluble Gly-TPA composite salts were characterized by a variety of analytical and spectroscopic techniques and exploited for esterification of palmitic acid with methanol.

2. Experimental section

2.1. Preparation of Gly-TPA catalysts

All research grade chemicals were used without further purification unless specified otherwise. The organic TPA salts were synthesized following the procedures similar to that reported earlier for the preparation of TPA-based sulfonated IL salts [15]. More specifically, ca. 2.88 g of TPA ($H_3PW_{12}O_{40}$) was first dissolved in 30 mL deionized water under vigorous stirring

at room temperature. To this solution, a desirable amount of aqueous glycine (Gly) solution was added drop wise while under continuous stirring. The mixture solution was allowed to stir at 363 K for 24 h. After removal of water, the resultant solid product was washed with diethyl ether, followed by drying under vacuum. As a result, a series of Gly-TPA catalysts, denoted as $[GlyH]_xH_{3-x}PW_{12}O_{40}$ (x = 1.0–3.0).

2.2. Catalyst characterization

All Fourier-transform infrared (FT-IR) spectra for samples in KBr disks were recorded on a Bruker IFS-28 spectrometer. X-ray diffraction (XRD) patterns were obtained by a Rigaku Ultimate IV diffractometer using Cu Kα radiation at 40 kV and 40 mA. Thermogravimetric and differential thermogravimetric (TG-DTG) measurements were performed on a Netzsch TG-209 thermal analyzer under a heating rate of 10 K/min. High-resolution solution-state ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra of various catalyst samples dissolved in deuterated dimethyl sulfoxide-d_6 (DMSO) were acquired on a Bruker-Biospin Avance III 500 spectrometer at a Larmor frequency of 500.13 and 125.76 MHz, respectively, using a single-pulse sequence. On the other hand, their corresponding solid-state ^{31}P magic-angle spinning (MAS) NMR spectra were acquired at a Larmor frequency of 202.46 MHz using a single-pulse sequence under the conditions: pulse-width ($\pi/6$), 1.5 μs; recycle delay, 10.0 s; sample spinning rate, 12 kHz. The ^{31}P chemical shifts ($\delta^{31}P$) were referenced to that of 85% H_3PO_4 aqueous solution. The detail of sample processing was prepared following the procedure outlined in literature [18].

2.3. Catalytic reaction

The catalytic activity of various catalysts were tested by esterification of palmitic acid (PA) with methanol (MeOH). All reactions were carried out in a 100 mL three-necked flask equipped

with a thermometer, a magnetic stirrer, a reflux condenser, and a drop funnel (containing 3A molecular sieves). The latter was exploited to remove water produced during the esterification reaction. The reaction mixture was heated to reflux for a desired period of time in an oil bath kept at a fixed temperature under continuous stirring, then, cooled to RT. Subsequently, the catalyst was separated from the reaction mixture, followed by washing with diethyl ether for reuse. The reaction products were analyzed by gas chromatography (GC; Agilent 6890N) equipped with a flame-ionization detector (FID) through a HP-5 capillary column. Reactants and products were identified by comparing with authentic samples. Methyl laurate was used as the internal standard. The conversion of palmitic acid was derived from the equation:

$$\text{Conversion (\%)} = (1 - a_1/a_2) \times 100\ \% \qquad (1)$$

where a_1 and a_2 represents the initial and final acidity of the reaction mixture, respectively. The acidity values were monitored by titration with sodium hydroxide (NaOH).

3. Results and discussion

3.1. Characterization of catalysts

FT-IR spectra of the glycine (Gly), pristine TPA ($H_3PW_{12}O_{40}$), and various $[GlyH]_xH_{3-x}PW_{12}O_{40}$ (x = 1.0–3.0) catalysts were compared in Fig. S1 (Supplementary data). The pristine TPA showed the typical characteristic bands for Keggin structure at ca. 3435, 1080, 983, 889, and 804 cm^{-1}, which may be assigned due to asymmetric stretching vibration of O–H, P–O, terminal W=O, corner-sharing W–O_b–W, edge-sharing W–O_c–W, respectively [19]. For all Gly-TPA composite salts, in spite of notable decreases in peak intensities and slight shifts in peak positions, the five aforementioned characteristic bands responsible for TPA remained visible, indicating the preservation of Keggin structure even after substitution of protons by the organic

$[GlyH]^+$ cations. Moreover, additional vibrational bands at 1745 and 2750–3300 cm^{-1} were also observed, which may be attributed to C=O stretching from the carboxyl groups and N–H stretching originated from Gly, respectively. These observation, together with the increasing peak intensity of the 1745 cm^{-1} band with increasing Gly loading, verify that the structures of both organic $[GlyH]^+$ cation and inorganic polyanions ($PW_{12}O_{40}^{3-}$; PW) associated with these hybrid ionic catalysts were well preserved and were successfully linked together.

Fig. S2 (Supplementary data) shows the corresponding XRD patterns obtained from various samples. The XRD profile of the parent TPA in Fig. S2a (Supplementary data) revealed the featured diffraction peaks at 10.3°, 25.3°, and 34.6° for the Keggin-type structure with long range ordering [20]. Upon incorporating Gly onto TPA, while the Gly-TPA catalysts exhibited XRD patterns similar to that of the pristine TPA, a marginal shift of diffraction peaks toward higher 2θ values was observed along with additional weaker peaks. However, no diffraction peaks associated with Gly (Fig. S2b; Supplementary data) could be identified, suggesting the presence of a new organic salt phase with good crystallinity. Further increasing the concentration of Gly (i.e., increasing x value) led to notable decreases in crystallinity, which were accompanied by emerging of additional peaks in 2θ region of ca. 5.0–10.0°. These results, which coincide with FT-IR data, indicate that a strong coupling between the organic $[GlyH]^+$ cation and inorganic PW anions did occur in the Gly-TPA catalyst. Again, a successful incorporation of Gly onto TPA may be inferred.

The thermal property of the Gly-TPA catalysts were examined by means of TG-DTG. Since all $[GlyH]_xH_{3-x}PW_{12}O_{40}$ (x = 1.0–3.0) samples showed a similar TG-DTG profile over the temperature range of RT–823 K, herein, only the curve observed for the $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ (x

= 1.0) sample was illustrated and discussed. It was found that, while the parent glycine exhibited a weight-loss peak at 528 K (Fig. S3a; Supplementary data), the pristine TPA showed multiple peaks at 339, 458, 666, and 787 K (Fig. S3b; Supplementary data), which may be ascribed due to desorption of physisorbed water, loss of crystalline water, and collapses of Keggin structure (666 and 787 K), respectively. By comparison, only two major desorption peaks were observed for the $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ catalyst (Fig. S3c; Supplementary data). The weight-loss peak appeared at 458 K may be attributed unambiguously to the loss of crystalline water, whereas the peak at 587 K should be most likely due to the decomposition of organic species in the Gly-TPA catalyst. These results obtained from thermal gravimetric analysis thus further demonstrated that PW anions were indeed successfully anchored with $[GlyH]^+$ cations, and remained stable over the range of temperature (333–383 K; *vide infra*) employed for the catalytic studies.

On the other hand, acidic properties of pristine TPA, Gly, and various Gly-TPA catalysts were characterized by the solid-state ^{31}P-TMPO NMR approach (*vide supra*), which has been demonstrated as a powerful technique for acidic characterization of solid [18] and liquid [15–17] acid catalysts. This is made possible by the fact that a linear correlation between the observed ^{31}P NMR chemical shifts and the strengths of Brønsted acidity may be inferred [18]. Upon adsorption on to the acid catalyst, the basic TMPO molecules tend to interact with the Brønsted acidic protons to form $TMPOH^+$ complexes, giving rise to a distribution of ^{31}P resonances whose chemical shifts increase with increasing acidic strengths of the acid sites. As demonstrated in our earlier reports [20], the ^{31}P NMR spectrum of TMPO adsorbed on TPA typically exhibits multiple ^{31}P signals with chemical shifts (CSs; δ^{31}P) within the range of 40–95 ppm. In addition to the physisorbed TMPO, which normally appears at a δ^{31}P of ca. 40 ppm. The δ^{31}P responsible for

TMPO adsorbed on Brønsted acid sites in TPA may be divided into three regions, namely region I (85–95 ppm), region II (75–85 ppm), and region III (55–75 ppm) [20]. The ^{31}P signals in regions I and III may be assigned due to $TMPOH^+$ and $(TMPO)_2H^+$ adducts, respectively, whereas those in region II were attributed to distorted $TMPOH^+$ adducts in the presence of spatial hindrance. As the TMPO-loaded TPA sample was subjected to proper thermal treatment ($T \geq 423$ K), only three overlapped ^{31}P resonance signals in region I remained visible, these peaks at ca. 92, 89, and 87 ppm were ascribed due to TMPO adsorbed on the three available H^+ sites of TPA (i.e., $H_3PW_{12}O_{40}$). Further study by density functional theory (DFT) calculations revealed that TMPO probe molecules prefer to interact with Brønsted acid protons locate at terminal oxygen sites of the PW polyanions [20]. Moreover, it has been demonstrated that a threshold for superacidity of 86 ppm may be inferred based on the ^{31}P-TMPO NMR approach [19], that all three ^{31}P resonances observed for pristine TPA revealed $\delta^{31}P$ exceeding 86 ppm indicate that all Brønsted protons (H^+) indeed possess superacidic strengths.

Fig. 1 shows the ^{31}P MAS NMR spectra of TMPO absorbed on TPA, Gly and various Gly-TPA catalysts. The ^{31}P-TMPO spectrum of pristine TPA exhibited overlapped signals spanned over the $\delta^{31}P$ range of 55–95 ppm in addition to the peaks at ca. –10.8 and –15.0 ppm. The latter peaks may be unambiguously attributed to ^{31}P resonance of the PW Keggin framework [11,20,21]. Similar to that observed for the pristine TPA [20], the peaks appeared in the $\delta^{31}P$ range of ca. 75–95 ppm (regions I and II) may be attributed to the presence of $TMPOH^+$ complexes, whereas the peaks within 55–75 ppm may be assigned due to two TMPO molecules adsorbed on a H^+ site, i.e., signals arose from $(TMPO)_2H^+$ adducts [21]. The latter may be provoked by the "pseudo liquid" characteristics of TPA secondary structure [11,20]. In other word, transport of the

TMPO guest molecules in the PW matrix may invoke a desorption/absorption process associated with the $(TMPO)_nH^+$ ($n \geq 2$) adducts.

Upon anchoring TPA onto Gly, in addition to the peaks arising from the PW anions themselves (which are irrelevant to the acidic properties of Gly-TPA catalyst), notable broadening of ^{31}P peaks responsible for the $TMPOH^+$ and $(TMPO)_2H^+$ adducts were evident (Figs. 1b–1d). In particular, resonances that originally accounted for presence of superacidic H^+ sites of pristine TPA (i.e., peaks at ca. 88.6 and 92.2 ppm; Fig. 1a) tend to decrease with increasing Gly/TPA molar ratio (x). These peaks eventually diminished as x reached 3.0 (i.e., for the $[GlyH]_{3.0}PW_{12}O_{40}$; Fig. 1d), leaving a broad resonance peak at ca. 60 ppm. By comparison, the parent Gly exhibited only a single sharp peak at 41.8 ppm (Fig. 1e). Thus, it is indicative that the acidic strengths of various $[GlyH]_xH_{3-x}PW_{12}O_{40}$ (x = 1.0–3.0) catalysts decrease with increasing x value. In other words, progressive incorporation of Gly tends to gradually eliminate the available protic sites, which provokes an effective average of Brønsted acidic strength in the Gly-TPA catalysts, thus, results in lowering of the overall acidity. Nonetheless, progressive elimination of protic sites also promotes segregation of TPA Keggin units, which is favorable for molecular transport; similar phenomenon was also observed in our previous study for a TPA-based sulfonated ionic liquid system [15].

3.2. Esterification of palmitic acid with methanol

The catalytic activities of the pristine TPA, Gly, and various Gly-TPA catalysts during esterification of PA with MeOH were also examined. Esterification, which invokes reaction between FFA (carboxylic acids) and alcohols, is known to be a typical acid-catalyzed reaction. It is noteworthy that the $[GlyH]_xH_{3-x}PW_{12}O_{40}$ (x = 1.0–3.0) catalysts are highly soluble in water and polar solvents but immiscible with apolar esters. Thus, the reaction system is strictly

homogeneous during the early stage of esterification reaction due to complete dissolution of the organic Gly-TPA salt catalyst in methanol and water. As the reaction proceeded, the reaction mixture gradually became turbid milky. Upon completing the reaction under continuous water-removal scheme, the high yield of esters provoked the occurrence of spontaneous self-separation between the products and the organic salt catalyst, forming a biphasic liquid layers. It is noteworthy that since an excessive amount (8–16 folds) of MeOH was adopted than PA during the esterification reaction, substantial amount of excessive MeOH still retained in the reaction mixture even after a complete PA conversion was reached. Thus, the excessive MeOH (which simultaneously served as the co-feed, the solvent, as well as the water-carrying agent) in the filtrate was distilled. Subsequently, the upper organic layer containing methyl palmitate as the primary product may be removed easily by suction, while the colloidal Gly-TPA catalyst residing in the bottom layer may be recycled after simple filtering and washing treatments. Similar results have also been found in esterification reaction over other types of organic TPA-based salt catalysts [15–17].

The catalytic performances of various catalysts during esterification of PA with MeOH are summarized in Table 1. The parent Gly, which possesses only weak Brønsted acidity (*cf.* Fig. 1e), showed inferior activity for catalyzing esterification reaction. Nonetheless, it tends to form $GlyH^+$ complexes with Brønsted acidic protons in the presence of TPA, leading to a Gly-TPA composite catalyst with strong acidity. In terms of the biodiesel (primarily methyl palmitate) yield, the catalytic activity of these organic salt catalysts were found to follow the trend: $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ > $[GlyH]_{2.0}H_{1.0}PW_{12}O_{40}$ > pristine TPA ($H_3PW_{12}O_{40}$) > $[GlyH]_{3.0}PW_{12}O_{40}$. Among them, the $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ (x = 1.0) catalyst exhibited the best catalytic activity with

an ester yield of 93.3%. As mentioned above, the incorporation of Gly, though tends to eliminate the available protic sites in TPA, also helped to serve as a spacer to promote segregation of PW polyanions, which in turn, rendering better mass transport during the esterification reaction [11,21]. Together with the Brønsted acid H^+, the $GlyH^+$ complexes also serve to balance the charge of the PW polyanions. In this context, though exhibited a highest acidic strength (*cf.* Fig. 1a), the pristine TPA may be handicapped by the transport resistance. As a result, the three available Brønsted acid protons (H^+) may not be fully accessible to the reactants during esterification, leading to only a modest catalytic activity. On the other hand, as the Gly/TPA molar ratio reached 1:1 (i.e., x = 1.0), while one of the protonic site was occupied by Gly to favor anchoring of organic and inorganic moieties and the subsequent molecular transport, two strong Brønsted H^+ remained available (Fig. 1b) for catalyzing the reaction. Consequently, this led to an optimal ester yield over the $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ catalyst. However, as the Gly/TPA ratio (x value) was further increased, a notable decrease in overall Brønsted acidity of Gly-TPA catalysts (Figs. 1c–1d) due to progressive decrease in available protic sites was observed, leading to gradual lowering of their catalytic activities.

To afford optimization of experimental variables, namely molar ratio of the reactants, amount of catalyst, reaction time, and reaction temperature, a more detailed investigation was conducted using the $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ sample as the standard catalyst, and relevant results are depicted in Fig 2. Again, to ensure a complete conversion of PA and high esters yield during the esterification, the reaction was carried out under excessive amount of MeOH, which simultaneous served as the reactant, solvent, and water-carrying agent. As shown in Fig. 2a, a strong correlation between the biodiesel yield and reactants molar ratio was observed, leading to an optimal yield at

MeOH/PA = 12. Thus, an excessive amount of MeOH than PA is favorable for shifting the reversible esterification reaction towards the production of biodiesel. On the other hand, upon increasing MeOH/PA > 12, the lowering of the esters yield was observed due to dilution effect. Thus, an optimal MeOH/TPA molar ratio of 12 was adopted for further studies.

The effect of catalyst amount on catalytic performance during esterification of PA with MeOH over the $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ catalyst was examined over fixed reaction conditions (MeOH/PA = 12; reaction time = 3 h; temperature = 363 K) under varied Gly-TPA salt from 4–8 wt% relative to the acid, as shown in Fig. 2b. Clearly, as catalyst amount increased from 4 to 6 wt%, the biodiesel yield also increased from ca. 84% to 93% due to increase in available strong acid sites. However, as the amount exceeded 6 wt%, an inferior catalytic activity was observed. It is anticipated that the presence of excessive amount of catalyst should provoke a faster reaction equilibrium, which may be accompanied by undesirable side reactions that eventually led to lowering of esters yield. Thus, the most suitable catalyst amount for an optimal operation of the present esterification reaction system should be ca. 6 wt%.

On the other hand, the effect of reaction time on biodiesel yield was investigated by varying the reaction time from 0.5 to 4.0 h while keeping other variables unchanged (MeOH/PA = 12, catalyst amount = 6 wt%, and reaction temperature = 363 K). As shown in Fig. 2c, the biodiesel yield gradually increased with reaction time, reaching a maximum yield of 93.3% at 3 h. However, further increase in reaction time led to a notable decrease in biodiesel yield. This verifies that esterification reaction is an equilibrium reaction and that esters product may react with water continuously formed during the reaction, leading to lowering of biodiesel yield at prolonged reaction time (> 3 h). Considering other relevant issues such as production cost and energy

consumption during the esterification process, an optimal reaction time of 3 h was chosen for further study.

Finally, the role of reaction temperature, which is one of the key factors affecting the catalytic performance, was also examined. A lower reaction rate is anticipated for reaction carried out at a lower temperature, while undesirable side reactions may take place at higher reaction temperatures to spoil the product selectivity. As shown in Fig. 2d, the biodiesel yield increased with increasing reaction temperature, reaching 93.3 % at 363 K over a reaction time of 3.0 h. The product yield so obtained was much higher than that of 88.5 % obtained in the absence of water removal. Again, the higher product yield is attributed to the more effective blending of reactants at higher temperatures and that the water by-product being removed continuously from the system along with the water-carrying agent (MeOH), thus, shifting the reaction equilibrium towards formation of biodiesel. However, notable decreases in PA conversion and biodiesel yield were observed upon further increasing the reaction temperature above 363 K.

In summary, the optimal reaction conditions during esterification of PA with MeOH over the $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ catalyst are: MeOH/PA = 12, catalyst amount = 6 wt%, reaction time = 3 h, and reaction temperature = 363 K. Under the optimal conditions, $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ catalyst showed excellent stability and recyclability, the biodiesel yield only dropped ca. 4–5% after six repeated cycles (Fig. 3). Thus, it is conclusive that the $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ organic salt is a durable catalyst suitable for practical applications in conversion of biomass to chemicals.

4. Conclusions

A series of $[GlyH]_xH_{3-x}PW_{12}O_{40}$ (x = 1.0–3.0) organic salts have been successfully synthesized and exploited for catalytic conversion of free fatty acids. Acidity characterization

utilizing the ^{31}P-TMPO NMR approach revealed that $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ catalyst was found to possess superacidic characteristics similar to the pristine bulk TPA, leading to the highest observed activity and an optimal biodiesel yield (93.3%). The $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ catalyst could be reused several times without much loss in catalytic activity, indicating that the Gly-TPA organic salts are truly efficient and reusable catalysts suitable for practical industrial applications for conversions of biomass to chemicals.

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Table 1

List of biodiesel yield during esterification of palmitic acid with methanol over various catalysts. [a]

Catalyst	Methyl palmitate yield (%)[b]
Glycine (Gly)	Nil
$H_3PW_{12}O_{40}$ (TPA)	86.7
$[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$	93.3
$[GlyH]_{2.0}H_{1.0}PW_{12}O_{40}$	87.2
$[GlyH]_{3.0}PW_{12}O_{40}$	81.2

[a] Reaction conditions: MeOH/PA = 12:1; amount of catalyst 6 wt%; reaction time 3 h; temperature 363 K.

[b] Analyzed by GC.

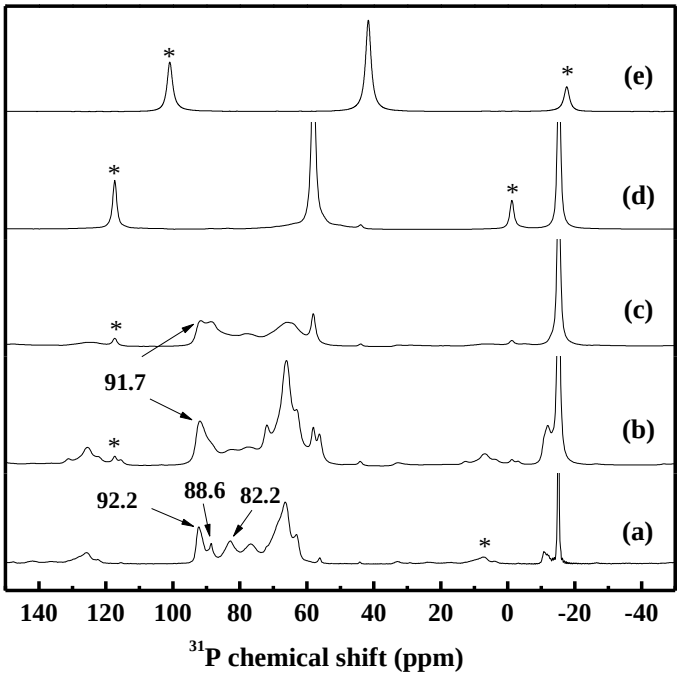

Fig. 1. Solid-state ^{31}P MAS NMR spectra of TMPO adsorbed on (a) pristine TPA, (b) $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$, (c) $[GlyH]_{2.0}HPW_{12}O_{40}$, (d) $[GlyH]_{3.0}PW_{12}O_{40}$, and (e) Gly. The asterisks denote spinning sidebands.

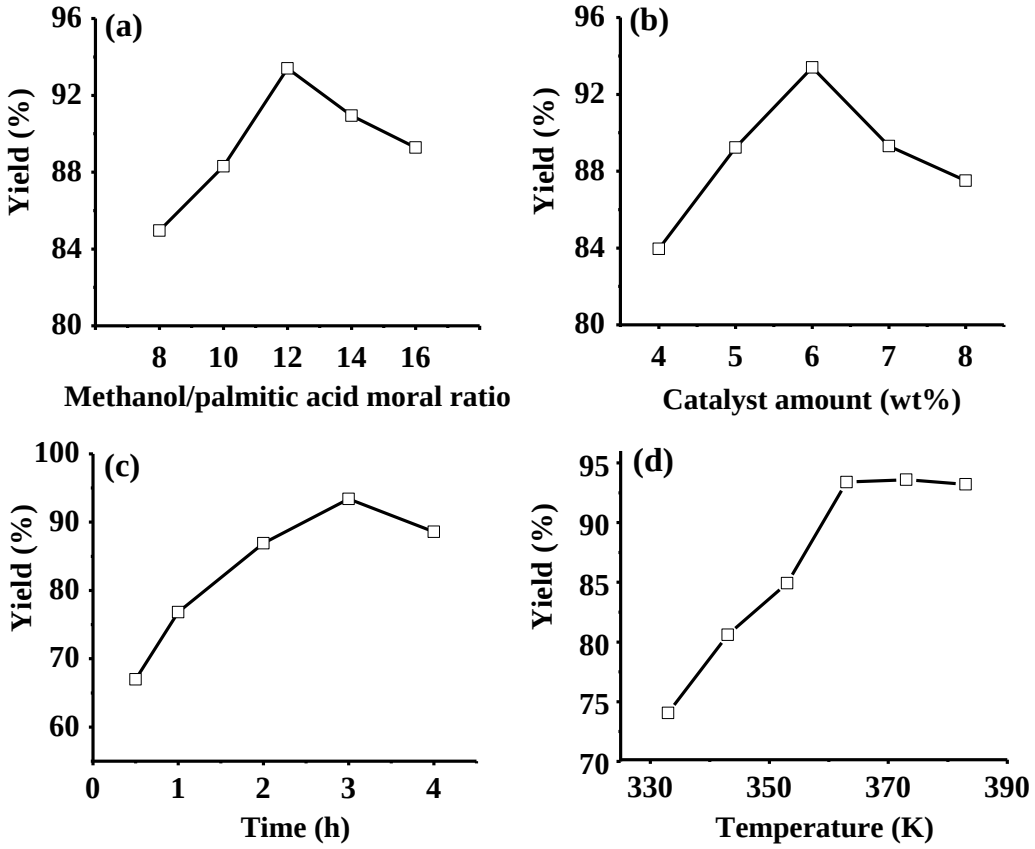

Fig. 2. Variations of biodiesel yield during esterification of palmitic acid with methanol over the $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ catalyst as a function of (a) MeOH/PA molar ratio, (b) catalyst amount, (c) reaction time, and (d) reaction temperature. Note that while varying each experimental variable, other parameters were kept constant at their predicted optimal values: MeOH/PA = 12:1, catalyst amount = 6 wt%, reaction time = 3.0 h, and reaction temperature = 363 K.

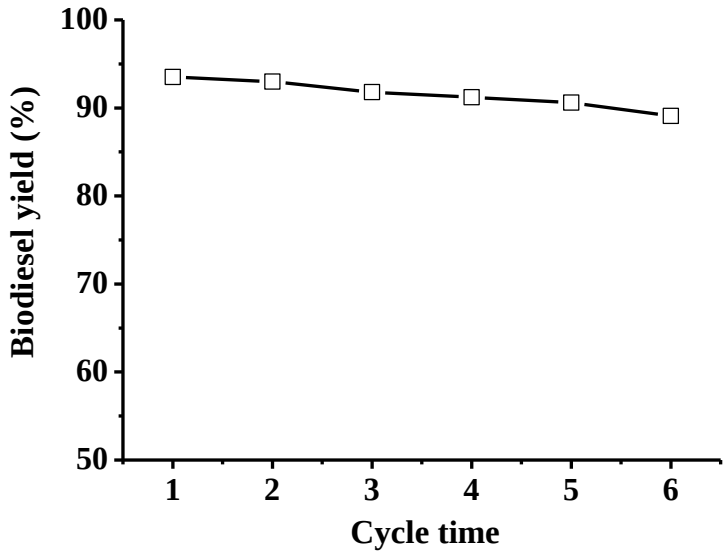

Fig. 3. Stability of the $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ catalyst during esterification of palmitic acid with methanol. Reaction conditions: palmitic acid, 0.03 mol; methanol, 0.36 mol; catalyst amount, 6 wt%; reaction time, 3 h; reaction temperature, 363 K.

Supplementary Material

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