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

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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.

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.
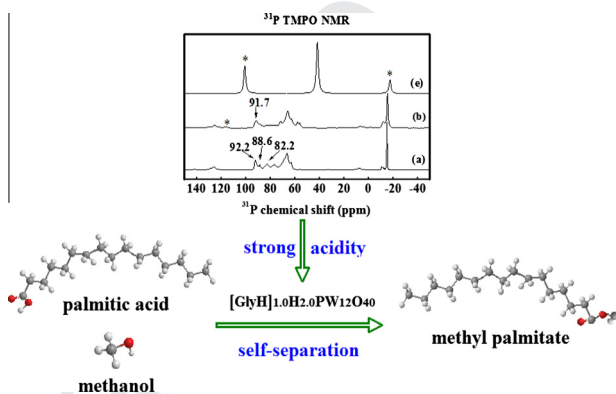
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ABSTRACT

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 ^1H 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%.

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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], and heteropolyacids (HPAs) [8,9], 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].

HPAs, 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 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. IR spectra of adsorbed pyridine (Py-IR) were recorded with the same apparatus. Each sample was pressed into a self-supporting wafer, then, degassed in a vacuum at 150 °C for 4 h. Subsequently, the catalyst was exposed to pyridine vapor at room temperature (RT; 25 °C) at first, then, slowly raising the temperature to 100 °C, maintained for about 1 h. Finally, the pyridine-loaded sample was cool to RT again. The Py-IR spectra were then recorded at RT after removing physisorbed pyridine by a vacuum for 1 h. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al Kα radiation. 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. Field-emission scanning electron microscopy (FE-SEM) measurements were conducted on a Hitachi SU 8010 microscope. Elemental analyses were carried out on an ICP-OES CID spectrometer (iCAP 6500; Thermo Scientific). High-resolution solution-state ^1H 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 may be derived from the equation:

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