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Efficient conversion of renewable levulinic acid to *n*-butyl levulinate catalyzed by ammonium and silver co-doped phosphotungstic acid

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ABSTRACT

Ammonium and silver co-doped phosphotungstic acid was developed as novel efficient catalyst for the synthesis of *n*-butyl levulinate. The catalyst was characterized by element analysis, FT-IR, XRD and Hammett indicator method. Among them, $(NH_4)_{0.5}Ag_{0.5}H_2PW_{12}O_{40}$ exhibited the highest catalytic activity, and the yield of *n*-butyl levulinate could reach up to 99.0% within 2 h. The results showed that the activity of $(NH_4)_{0.5}Ag_{0.5}H_2PW_{12}O_{40}$ was higher than that of single Ag^+ or NH_4^+ doped H_3PW and other representative catalysts reported by literatures. In addition, $(NH_4)_{0.5}Ag_{0.5}H_2PW_{12}O_{40}$ performed good reusability for this reaction.

1. Introduction

Levulinic acid (LA) is a platform organic chemical and one of the top 12 building blocks that can be obtained from the deconstruction of lignocellulosic biomass. It can be used for preparing numerous useful chemicals such as levulinate esters, γ-valerolactone, acrylic acid, etc. Among them, levulinate esters have been widely used as additives in gasoline and biodiesel since its low toxicity, high lubricity, flash point stability and moderate flow properties under low temperature [1–3].

Generally, levulinate esters are synthesized by the esterification of LA with alcohols using mineral acid or organic sulfonic acid as catalyst [4]. However, these methods suffer from high cost separation, large energy consumption, equipment corrosion and environmental pollution. A large number of heterogeneous catalysts have been also reported for the synthesis of levulinate esters such as zeolites [5–9], sulfonic materials [10–14], MOFs [15], heteropoly acids (HPAs) and supported HPAs [16,17]. Among them, HPAs are known to be excellent catalysts for a wide range of acid-catalyzed reactions. However, HPAs have the draw backs of high solubility in polar media, low surface area and relatively low thermal stability. Recently, Dharne and Bokade have developed dodecatungestophosphoric acid supported on K10 as catalyst for the synthesis of *n*-butyl levulinate [16]. Although 97% LA conversion can be obtained, the activity of catalyst decreased after two recycles due to the increasing leaching of dodecatungestophosphoric acid from K10 support.

Compared to grafting HPAs onto porous supports, it is more effective to exchange H^+ of HPAs with different cations (e.g., K^+, Cs^+, Ag^+) to form insoluble salts, which can tube and enhance the activity of HPAs [18–20]. Different simple salts based on only one type of cation (excluding H^+) have been extensively reported [18]. For example, silver-doped phosphotungstic acid (Ag_1H_2PW) has been developed as efficient heterogeneous catalyst for the esterification [21], etherification [22], transesterification [23], and so on. However, different cations co-doped HPAs have been rarely reported in the literature.

Herein, ammonium and silver co-doped phosphotungstic acid was prepared and used as efficient catalyst for the conversion of renewable LA to *n*-butanol levulinate. To the best of our knowledge, there are no reports available for the esterification of LA with *n*-butanol in the presence of different cations co-doped HPAs.

2. Experimental

2.1. Preparation and characterization of catalysts

In a typical procedure for the preparation of ammonium and silver co-doped phosphotungstic acid catalysts, $H_3PW_{12}O_{40}$ (H_3PW, 0.18 mol/L) was dissolved in deionized water with vigor-

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ous stirring at room temperature. Then, the appropriate amount of $(NH_4)_2CO_3$ (0.03 mol/L) aqueous solution was added dropwise to the H_3PW aqueous solution, followed by the addition of $AgNO_3$ (0.06 mol/L) aqueous solution. The resultant mixture was further stirred for 2 h at room temperature. Finally, the solid sample was obtained by filtration, dried at 80 °C overnight, and calculated at 200 °C in air for 4 h. These prepared catalysts were designated as $(NH_4)_xAg_yH_{3\text{-}x\text{-}y}PW$ ($x = 0.5, 1, 2, y = 0.5, 1, 2$).

Nitrogen content was detected in a Perkin-Elmer EA 2400 II. The content of Ag and W was obtained by X-ray fluorescence in a Shimadzu EDX 720 spectrometer with a rhodium X-ray source tube. The XRF spectra were collected under vacuum conditions setting the X-ray source at 50 kV. The detection was performed on flake sample which was prepared by tabletting of powder. The X-ray diffraction patterns (XRD) were collected on X-ray diffractometer (XPERT PRO) using a Cu K radiation source ($\lambda = 1.54056$ Å), operating at 40 kV and 45 mA. The diffractographs were recorded in the range of 10–70° with a scan rate of 5°/min and step size of 0.03°. FT-IR spectra were obtained by Nicolet 560 in KBr pellets. The surface areas of catalysts were measured by nitrogen adsorption and desorption on a TriStar II 3020 (Micromeritics Instrument Corporation) at 77 K and determined by using the BET methods. The acidity of catalysts was determined by means of *n*-butylamine titration using Hammett indicators. The catalyst leaching in filtration was detected by TS IRIS 1000 ICP-AES instrument.

2.2. *Typical procedure for the esterification of LA with* n*-butanol*

Typical procedure for the synthesis of *n*-butanol levulinate: 11.6 g (0.1 mol) LA, 14.8 g (0.2 mol) *n*-butanol and 0.174 g catalyst were charged into a 100 mL flask equipped with a magnetic stirring, a reflux condenser and a water segregator. The reaction mixture was then heated to desired temperature with continuous stirring for 2 h. After the reaction, the mixture was cooled to room temperature. Solid catalyst was separated from product by filtration. And the product was analyzed by GC (Shandong Lunan Ruihong Co., SP-6890). The structure of the product was defined by GC–MS (HP 6890/5973). In the experiment to test the reusability of catalyst, $(NH_4)_{0.5}Ag_{0.5}H_2PW$ was separated by filtration, washed by ethanol, dried at 90 °C and reused for the next run.

3. Results and discussion

3.1. *Characterization of catalysts*

Although much care was taken to match the theoretical values during preparation, it was important to detect the actual compositions of catalysts. The element content of Ag_1H_2PW, $(NH_4)_1H_2PW$ and $(NH_4)_{0.5}Ag_{0.5}H_2PW$ is summarized in Table 1. The actual element content of catalysts was close to the calculated values, which indicated that the preparation methodology was effective for controlling the desired stoichiometry of above catalysts.

Ag_1H_2PW and $(NH_4)_{0.5}Ag_{0.5}H_2PW$ were characterized by FT-IR spectra. It is well known that the Keggin anion of parent H_3PW consists of a central phosphorous atom tetrahedrally coordinated by four oxygen atoms and surrounded by twelve octahedral WO_6 units that share edges and corners in the structure. As shown in Fig. 1, the characteristic bands of typical Keggin anions can be clearly observed in the spectra of Ag_1H_2PW and $(NH_4)_{0.5}Ag_{0.5}H_2PW$. They are the bands located at 1080 cm^{-1} (ν_{as} P–O$_a$), 982 cm^{-1} (W–O$_d$), 890 cm^{-1} (ν_{as} W–O$_b$–W), and 807 cm^{-1} (W–O$_c$–W), respectively. The results indicate that the Keggin structure is maintained on ammonium and silver co-doped H_3PW catalyst. In addition to these bands, there is also a band related to N—H stretching observed at 1414 cm^{-1} for $(NH_4)_{0.5}Ag_{0.5}H_2PW$. It means that NH_4^+ still exists in $(NH_4)_{0.5}Ag_{0.5}H_2PW$ even after calculating at 200 °C for 4 h.

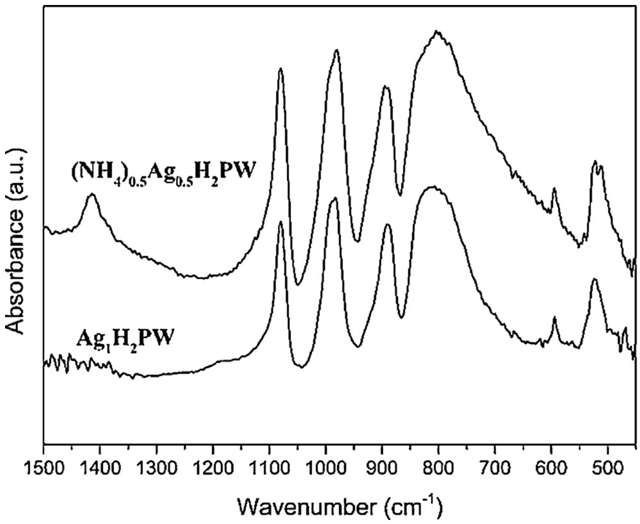

Fig. 1. FT-IR spectrum of Ag_1H_2PW and $(NH_4)_{0.5}Ag_{0.5}H_2PW$.

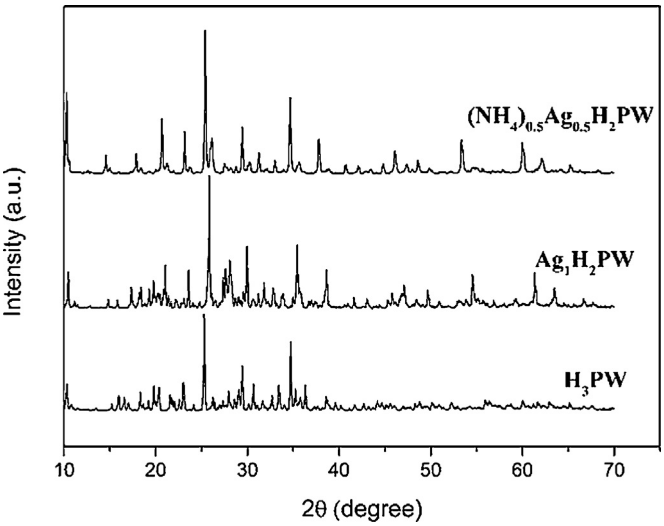

Fig. 2. XRD patterns of H_3PW, Ag_1H_2PW and $(NH_4)_{0.5}Ag_{0.5}H_2PW$.

Table 1
Element analysis of Ag_1H_2PW, $(NH_4)_1H_2PW$ and $(NH_4)_{0.5}Ag_{0.5}H_2PW$.

Catalyst	N (%)		Ag (%)		W (%)	
	Cal.	test	Cal.	test	Cal.	test
Ag_1H_2PW	–	–	3.62	3.56	73.86	72.52
$(NH_4)_1H_2PW$	0.62	0.57	–	–	76.15	74.37
$(NH_4)_{0.5}Ag_{0.5}H_2PW$	0.29	0.27	1.83	1.79	75.00	74.56

The XRD patterns of parent H_3PW, Ag_1H_2PW and $(NH_4)_{0.5}Ag_{0.5}H_2PW$ catalysts are displayed in Fig. 2. The parent H_3PW shows typical diffraction pattern of body-centered cubic secondary structure of Keggin anion, with characteristic diffraction peaks at 10.3°, 25.3°, and 34.6° [21–23]. The most intense peak for H_3PW at 25.3° is also present in the XRD patterns of Ag_1H_2PW and $(NH_4)_{0.5}Ag_{0.5}H_2PW$ samples, although this peak had slightly shifted to higher 2θ values. This peak is present at 25.8° for Ag_1H_2PW, and 25.4° for $(NH_4)_{0.5}Ag_{0.5}H_2PW$. It is speculated that Ag_1H_2PW and $(NH_4)_{0.5}Ag_{0.5}H_2PW$ catalysts possess the same symmetry as parent H_3PW but with a contracted unit cell.

For the acid-catalyzed reactions, the surface acid strength and density play important roles in determining the catalytic prop-