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

Xi Zhou [a,*], Ze Xian Li [a], Chao Zhang [a], Xue Ping Gao [a], You Zhi Dai [a], Gong Ying Wang [b]

[a] Department of Biological and Chemical Engineering, Shaoyang University, Shaoyang 422000 Hunan, PR China
[b] Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, 610041 Sichuan, PR China

ARTICLE INFO

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.

© 2016 Elsevier B.V. All rights reserved.

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-

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 $(NH_4)_xAg_yH_{3-x-y}PW$ (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 (λ = 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.
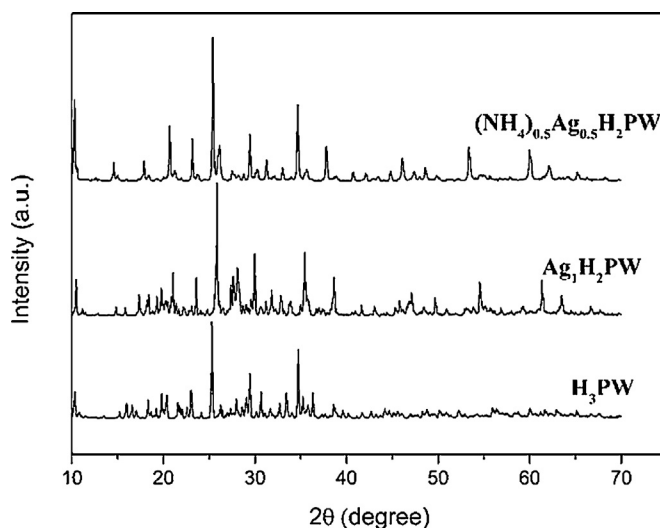
Ag_1H_2PW and $(NH_4)_{0.5}Ag_{0.5}H_2PW$ were characterized by FT-IR spectra. It is well known that the Keggin anion of parent H_3PW consists of a central phosphorous atom tetrahedrally coordinated by four oxygen atoms and surrounded by twelve octahedral WO_6 units

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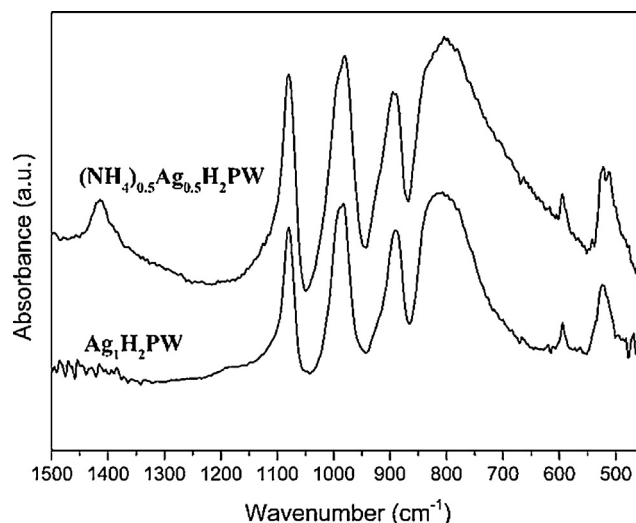
Fig. 1. FT-IR spectrum of Ag_1H_2PW and $(NH_4)_{0.5}Ag_{0.5}H_2PW$.

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

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.

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-

Table 2
Acid strength and acidity of Ag_1H_2PW and $(NH_4)_{0.5}Ag_{0.5}H_2PW$.

Catalyst	S_{BET} (m²/g)	H_0	Acidity (mmol/g)
H_3PW	5.1	$-12.70 < H_0 < -13.75$	1.62
Ag_1H_2PW	3.3	$-11.35 < H_0 < -12.70$	1.87
$(NH_4)_{0.5}Ag_{0.5}H_2PW$	10.8	$-11.35 < H_0 < -12.70$	2.01

Table 3
Effect of catalyst on the synthesis of n-butyl levulinate.

Entry	Catalyst	Yield (%)[a]	TOF (h⁻¹)[b]
1	–	34.2	–
2	H_3PW	96.8	32.3
3	Ag_1H_2PW	92.1	30.7
4	$(NH_4)_{0.5}Ag_{0.5}H_2PW$	99.0	33.0
5	$(NH_4)_1H_2PW$	95.5	31.8
6[c]	$(NH_4)_{0.5}Ag_{0.5}H_2PW$	75.2	75.2
7[c]	$(NH_4)_{0.5}Ag_{0.5}H_2PW$[d]	72.6	72.6
8	Ag_1H_2PW[d]	89.4	29.8
9	$(NH_4)_1H_2PW$[d]	75.6	25.2

Reaction conditions: LA: 0.1 mol, n-butanol: 0.2 mol, catalyst: 1.5% (Based on the mass of LA), 120 °C, 2 h.

[a] The selectivity of n-butyl levulinate was nearly 100% in all tests.
[b] Gram of LA converted per gram of catalyst in 1 h.
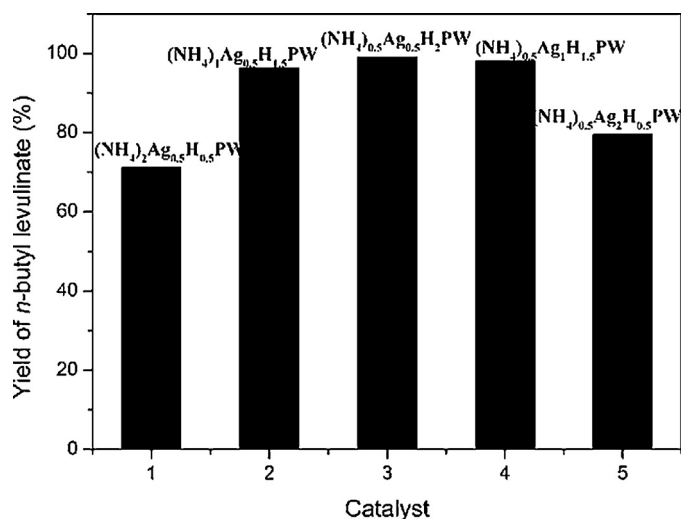[c] Catalyst: 0.5% (Based on the mass of LA).
[d] The 4th run.

erty. Therefore, Ag_1H_2PW and $(NH_4)_{0.5}Ag_{0.5}H_2PW$ catalysts were tested by the method of n-butylamine titration using Hammett indicators. As shown in Table 2, the surface acid strength (H_0) of Ag_1H_2PW and $(NH_4)_{0.5}Ag_{0.5}H_2PW$ was both in the range of -11.35 to -12.70, which was slightly lower than that of parent H_3PW. However, the surface acid density of Ag_1H_2PW (1.87 mmol/g) was higher than that of parent H_3PW (1.62 mmol/g), which was consistent with previous report [21]. Among them, $(NH_4)_{0.5}Ag_{0.5}H_2PW$ showed the highest surface acid density (2.01 mmol/g). Although the surface Brønsted acid sites of H_3PW salts was lower than that of parent H_3PW, H_3PW salts possess higher surface Lewis acid sites than H_3PW, as reported by previous literatures [21–23]. In addition, the surface area was one of the influence factors on the surface acid density. $(NH_4)_{0.5}Ag_{0.5}H_2PW$ showed the highest surface area among these catalysts, which might be one of reasons for its highest surface acid density.

3.2. Catalytic property test

Effect of catalyst on the conversion of renewable LA to n-butyl levulinate was investigated at 120 °C within 2 h. The reaction equilibrium was broken by removing water to improving the yield of n-butyl levulinate in all tests. As shown in Table 3, the yield of n-butyl levulinate was only 34.2% in the absence of catalyst. Then, the yield of n-butyl levulinate could reach 96.8% and 92.1% using H_3PW and Ag_1H_2PW as catalyst, respectively. Although the activity of H_3PW was higher than that of Ag_1H_2PW, H_3PW was completely dissolved in the reaction system resulting in a complicated process for catalyst recycling. In contrast to H_3PW, Ag_1H_2PW performed in heterogeneous state during the reaction, which was much more favorable in terms of sustainable chemistry.

As shown in Table 3, the yield of n-butyl levulinate was up to 99.0% with 33.0 turn over frequencies (TOF) value of LA using $(NH_4)_{0.5}Ag_{0.5}H_2PW$ as heterogeneous catalyst. And the results indicated that the activity of $(NH_4)_{0.5}Ag_{0.5}H_2PW$ is higher than that of Ag_1H_2PW. Although $(NH_4)_{0.5}Ag_{0.5}H_2PW$ and Ag_1H_2PW possessed similar Keggin structure and acid strength (Fig. 1, 2), the surface acid density of $(NH_4)_{0.5}Ag_{0.5}H_2PW$ was higher than that of Ag_1H_2PW (Table 2). It might be the reason for higher activity of $(NH_4)_{0.5}Ag_{0.5}H_2PW$. The activity of $(NH_4)_1H_2PW$ for the synthesis of n-butyl levulinate was also investigated. And its activity was

Fig. 3. Effect of dopant amount on the catalytic activity of $(NH_4)_xAg_yH_{3-x-y}PW$. Reaction conditions: LA: 0.1 mol, n-butanol: 0.2 mol, catalyst: 1.5% (Based on the mass of LA), 120 °C, 2 h.

also lower than $(NH_4)_{0.5}Ag_{0.5}H_2PW$. In addition, the selectivity of n-butyl levulinate was nearly 100% in all tests.

The reusability of solid acid catalyst was one of the key factors for evaluating its catalytic performance. Herein, the reusability of $(NH_4)_{0.5}Ag_{0.5}H_2PW$, Ag_1H_2PW and $(NH_4)_1H_2PW$ was investigated for the esterification of LA with butanol. The amount of $(NH_4)_{0.5}Ag_{0.5}H_2PW$ was decreased to 0.5% for the evaluation of its reusability, because the conversion of LA was too high (nearly100%) in the presence of 1.5% $(NH_4)_{0.5}Ag_{0.5}H_2PW$. As shown in Table 3, $(NH_4)_{0.5}Ag_{0.5}H_2PW$ performed good reusability. And the yield of n-butyl levulinate was decreased slightly from 75.2% in the first run to 72.6% in 4th run. The catalytic activity of Ag_1H_2PW had also no remarkable decrease after 4 runs, which was consistent with results reported by literatures [21–23]. However, the yield of n-butyl levulinate decreased quickly from 95.5% to 75.6% after 4 recycles of $(NH_4)_1H_2PW$. According to the literatures [18], the hydrophilicity of $(NH_4)_1H_2PW$ was better than that of Ag_1H_2PW, resulting higher loss of $(NH_4)_1H_2PW$ during the reaction in polar mixture. And the results of leaching test in filtration also proved that. The loss rate of $(NH_4)_1H_2PW$ was up to 18% after 4 runs, while the loss rate of $(NH_4)_{0.5}Ag_{0.5}H_2PW$ and Ag_1H_2PW was just about 2%. It should be one of reasons for poor reusability of $(NH_4)_1H_2PW$. Based on the results of activity and reusability test, $(NH_4)_{0.5}Ag_{0.5}H_2PW$ performed better catalytic property than traditional single NH_4^+ or Ag^+ doped H_3PW for the synthesis of n-butyl levulinate.

3.3. Effect of dopant amount on the activity of catalyst

The exchange number of H^+ in heteropoly acid had an important effect on the catalytic property of heteropoly acid salts. When the total doping amount of Ag^+ and NH_4^+ was setting in the range of 1–2.5, effects of doping amount of Ag^+ and NH_4^+ on the catalytic activity of $(NH_4)_xAg_yH_{3-x-y}PW$ were investigated in the present work. As shown in Fig. 3, the activity of $(NH_4)_xAg_yH_{3-x-y}PW$ decreased with increasing the total doping amount of Ag^+ and NH_4^+. Among these catalysts, $(NH_4)_{0.5}Ag_{0.5}H_2PW$ with remaining two H^+ in the molecular structure performed the highest activity, which was consistent with the results of Ag_1H_2PW [21].

3.4. Effect of catalyst dosage

Effects of catalyst dosage on the esterification of LA with n-butanol were investigated using $(NH_4)_{0.5}Ag_{0.5}H_2PW$ as catalyst.
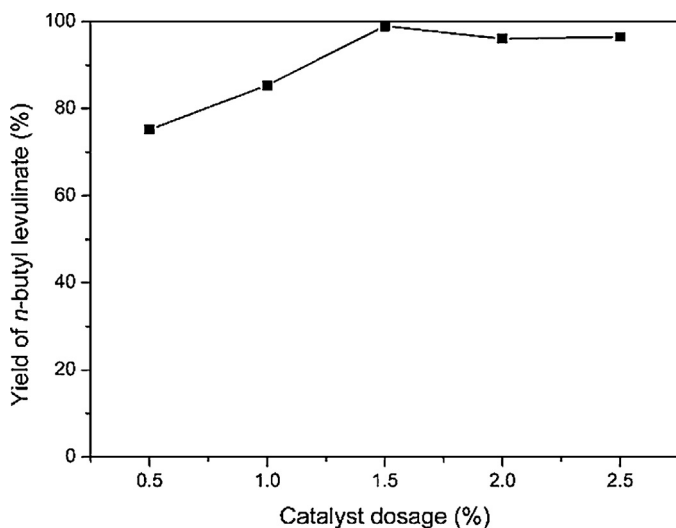
Fig. 4. Effect of catalyst dosage on the synthesis of n-butyl levulinate. Reaction conditions: LA: 0.1 mol, n-butanol: 0.2 mol, 120 °C, 2 h.
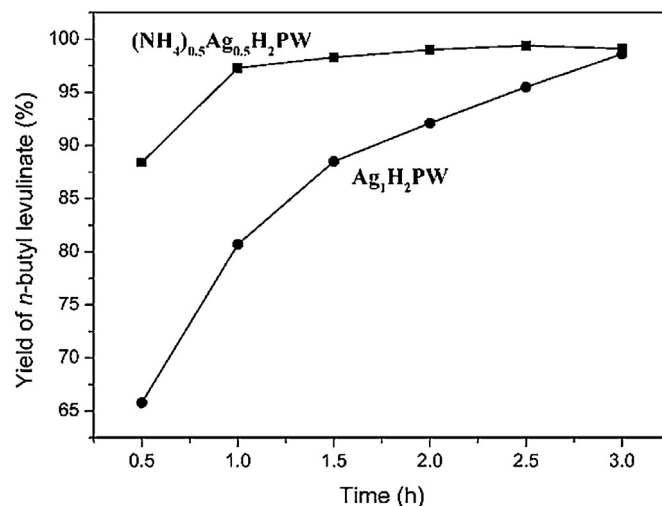

Fig. 6. Effect of reaction time on the synthesis of n-butyl levulinate. Reaction conditions: LA: 0.1 mol, n-butanol: 0.2 mol, catalyst: 1.5%, 120 °C.
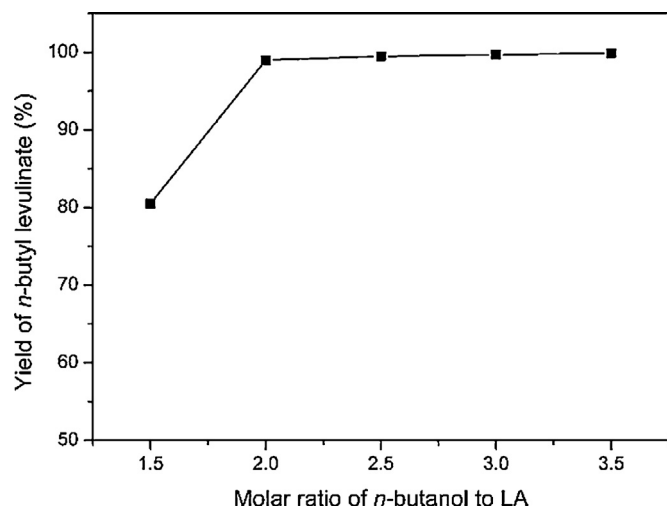
3.6. Effect of reaction time

In order to find out the detail progress of the reaction, effect of reaction time on the synthesis of n-butyl levulinate were studied using $(NH_4)_{0.5}Ag_{0.5}H_2PW$ and Ag_1H_2PW as catalyst, respectively. As shown in Fig. 6, the yield of n-butyl levulinate increased from 88.4% to 99.0% with increasing reaction time from 0.5 h to 2 h in the presence of $(NH_4)_{0.5}Ag_{0.5}H_2PW$. Then, n-butyl levulinate yield had no remarkable change with further prolonging reaction time to 3 h. It was worthy to note that n-butyl levulinate yield could reach up to 97.3% within 1 h. If Ag_1H_2PW was used as catalyst for the esterification of LA with butanol, the yield of n-butyl levulinate increased from 65.8% to 98.6% with increasing reaction time from 0.5 h to 3 h. And n-butyl levulinate yield was only 80.7% at 1 h. It proved that the catalytic activity of $(NH_4)_{0.5}Ag_{0.5}H_2PW$ was higher than that of Ag_1H_2PW.

3.7. Comparison of catalytic activity

Table 4 shows the results of activity evaluation of $(NH_4)_{0.5}Ag_{0.5}H_2PW$ and other representative solid acid catalysts reported by recently literatures for the esterification of LA with n-butanol. In order to solve the problem of low surface area and difficult separation for H_3PW, Dharne and Bokade [16] grafted H_3PW onto acid-treated clay (K10) and used it as solid acid catalyst for the synthesis of n-butyl levulinate. 97% n-butyl levulinate yield can be obtained in the presence of 20% (w/w) H_3PW/K10 with 10% catalyst amount in 4 h. The TOF value of LA was 12 h^{-1} calculating on the gram of H_3PW, which was lower than that using $(NH_4)_{0.5}Ag_{0.5}H_2PW$ as catalyst (33 h^{-1}). Recently, zeolite and metal-organic frameworks which possess high surface area have been applied in the synthesis of n-butyl levulinate, such as H-BEA zeolite, Micro/meso-HZ-5 and Zr-MOF [8,9,15]. In comparison with these catalysts, $(NH_4)_{0.5}Ag_{0.5}H_2PW$ also performed higher catalytic activity.

4. Conclusion

Among Ag^+ and NH_4^+ co-doped H_3PW catalysts, $(NH_4)_{0.5}Ag_{0.5}H_2PW$ performed the highest activity for the esterification of LA with butanol. In comparison with single Ag^+ doped H_3PW catalyst (Ag_1H_2PW), $(NH_4)_{0.5}Ag_{0.5}H_2PW$ showed the similar acid strength but higher surface acid density. And the catalytic activity of $(NH_4)_{0.5}Ag_{0.5}H_2PW$ was higher than that of Ag_1H_2PW,

Fig. 5. Effect of molar ratio of n-butanol to LA on the synthesis of n-butyl levulinate. Reaction conditions: LA: 0.1 mol, $(NH_4)_{0.5}Ag_{0.5}H_2PW$: 1.5%, 120 °C, 2 h.

As shown in Fig. 4, the yield of n-butyl levulinate increased quickly from 75.2% to 99.0% with increasing the amount of $(NH_4)_{0.5}Ag_{0.5}H_2PW$ from 0.5% (based on the mass of LA) to 1.5%, and then decreased slowly to 96.5% with further increasing the amount of $(NH_4)_{0.5}Ag_{0.5}H_2PW$ to 2.5%. Increase catalyst dosage up to 2.5% seems to have negative effect. It may be due to the existence of excess catalyst in the reaction system which may reduce the contact opportunity of LA and n-butanol.

3.5. Effect of material ratio

Esterification reactions are usually tested under an excess of alcohol to achieve higher yields. Herein, effect of material ratio on the synthesis of n-butyl levulinate using $(NH_4)_{0.5}Ag_{0.5}H_2PW$ as catalyst was studied with raising the ratio of n-butanol to LA from 1.5 to 3.5. As shown in Fig. 5, n-butyl levulinate yield increased quickly from 80.5% to 99.0% with increasing the ratio of n-butanol to LA from 1.5 to 2. And the yield of n-butyl levulinate increased slowly to 99.7% when the ratio of n-butanol to LA from reached 3.5. However, the amount of n-butanol at higher molar ratio results higher production cost. Thus, the ratio of n-butanol to LA was setting as 2.0 for the following experiments.

Table 4
Comparison of catalytic activity of $(NH_4)_{0.5}Ag_{0.5}H_2PW$ with representative catalysts reported in literatures.

Entry	Catalyst	Amount of catalyst (%)[a]	n (butanol):n (LA)	Time (h)	Yield (%)	TOF (h^{-1})[b]	Reference
1	$(NH_4)_{0.5}Ag_{0.5}H_2PW$	1.5	2:1	2	99.0	33	This work
2	$H_3PW/K10$	10	6:1	4	97	12[c]	[16]
3	H-BEA zeolite	10	7:1	4	82.2	2.1	[8]
4	Micro/meso-HZ-5	20	6:1	5	98	1.0	[9]
5	Zr-MOF	3	6:1	5	99	6.6	[15]

Reaction conditions: 120 °C.
[a] Based on the mass of LA.
[b] Gram of LA converted per gram of catalyst in 1 h.
[c] Calculated on the gram of H_3PW.

$(NH_4)_1H_2PW$ and other representative catalysts reported by recently literatures. When the molar ratio of LA to butanol was 1: 2, the yield of n-butyl levulinate could reach up to 99.0% in the presence of 1.5% $(NH_4)_{0.5}Ag_{0.5}H_2PW$ at 120 °C within 2 h. This work had certain significance for the development and application of different cation co-doped HPAs catalysts.

Acknowledgments

References

[1] G. Pasquale, P. Vázquez, G. Romanelli, G. Baronetti, Catal. Commun. 18 (2012) 115–120.
[2] J. Zhang, S.B. Wu, B. Li, H.D. Zhang, ChemCatChem 4 (2012) 1230–1237.
[3] K.Y. Nandiwale, V.V. Bokade, Environ. Prog. Sustain. Energy 34 (2014) 795–801.
[4] Y.H. Chung, T.H. Peng, H.Y. Lee, C.L. Chen, I.L. Chien, Ind. Eng. Chem. Res. 54 (2015) 3341–3354.
[5] H.J. Bart, J. Reidetschlager, K. Schatka, A. Lehmann, Ind. Eng. Chem. Res. 33 (1994) 21–25.
[6] D.R. Fernandes, A.S. Rocha, E.F. Mai, C.J.A. Mota, V.T.D. Mota, Appl. Catal. A: Gen. 425–426 (2012) 199–204.
[7] K.C. Maheria, J. Kozinski, A. Dalai, Catal. Lett. 143 (2013) 1220–1225.
[8] C.R. Patil, P.S. Niphadkar, V.V. Bokade, P.N. Joshi, Catal. Commun. 43 (2014) 188–191.
[9] K.Y. Nandiwale, V.V. Bokade, Chem. Eng. Technol. 38 (2014) 1–8.
[10] Y. Kuwahara, T. Fujitani, H. Yamashita, Catal. Today 237 (2014) 18–28.
[11] J.A. Melero, G. Morales, J. Iglesias, M. Paniagua, B. Hernández, S. Penedo, Appl. Catal. A: Gen. 466 (2013) 116–122.
[12] Y. Kuwahara, W. Kaburagi, K. Nemoto, T. Fujitani, Appl. Catal. A: Gen. 476 (2014) 186–196.
[13] B.L. Oliveira, V.T.D. Silva, Catal. Today 234 (2014) 257–263.
[14] F.D. Pileidis, M. Tabassum, S. Coutts, M.M. Titirici, Chin. J. Chem. 35 (2014) 929–936.
[15] F.G. Cirujano, A. Corma, F.X.L.I. Xamena, Chem. Eng. Sci. 124 (2015) 52–60.
[16] S. Dharne, V.V. Bokade, J. Nat. Gas Chem. 20 (2011) 18–24.
[17] K.Y. Nandiwale, S.K. Sonar, P.S. Niphadkar, P.N. Joshi, S.S. Deshpande, V.S. Patil, V.V. Bokade, Appl. Catal. A: Gen. 460–461 (2013) 90–98.
[18] S.S. Wang, G.Y. Yang, Chem. Rev. 115 (2015) 4893–4962.
[19] J.S. Santos, J.A. Dias, S.C.L. Dias, F.A.C. Garcia, J.L. Macedo, F.S.G. Sousa, L.S. Almeida, Appl. Catal. A: Gen. 394 (2011) 138–148.
[20] J.S. Santos, J.A. Dias, S.C.L. Dias, J.L. Macedo, F.A.C. Garcia, L.S. Almeida, E.N.C.B. Carvalho, Appl. Catal. A: Gen. 443–444 (2012) 33–39.
[21] S.H. Zhu, X.Q. Gao, F. Dong, Y.L. Zhu, H.Y. Zheng, Y.W. Li, J. Catal. 306 (2013) 155–163.
[22] Y.S. Ren, B. Liu, Z.H. Zhang, J.T. Lin, J. Ind. Eng. Chem. 21 (2015) 1127–1131.
[23] A. Zieba, L. Matachowski, J. Gurgul, E. Bielanska, A. Drelinkiewicz, J. Mol. Catal. A: Chem. 316 (2010) 30–34.