ORIGINAL PAPER

Synthesis of butyrate using a heterogeneous catalyst based on polyvinylpolypyrrolidone

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A heterogeneous polyvinylpolypyrrolidone supported Brønsted acidic catalyst ([PVPP-BS]HSO₄) was used to synthesize butyrate in this paper. The prepared catalysts were characterized by FT-IR, TG, and FESEM and their catalytic activity in butyric acid esterification with benzyl alcohol was investigated. The influencing factors such as the amount of catalyst, reaction temperature, and reaction time were carefully studied. Under the optimized condition with the butyric acid to benzyl alcohol mole ratio of 1 : 1.2 and the reaction temperature of 130 °C, the yield of benzyl butyrate reached 96.8 % within 4 h in the presence of 8 mass % of catalyst. Moreover, the catalyst could be reused six times without noticeable drop in activity. This catalyst was also used to synthesize other kinds of butyrates achieving the butyrate yield above 90 %. (© 2015 Institute of Chemistry, Slovak Academy of Sciences

 ${\bf Keywords:}\ {\rm butyrate,\ esterification,\ polyvinyl polypyrrolidone,\ catalyst}$

Introduction

Butyrate, as an alternative of the conventional intermediate in chemical industry, has drawn considerable attention in recent years due to its biodegradability and toxicity. Generally, butyrate is produced by butyric acid esterification with alcohols catalyzed by homogeneous catalysts such as H_2SO_4 and H_3PO_4 , which suffer from corrosiveness, difficult recovery and environmental hazards. To overcome the above problems, the development of solid acid catalysts such as acidic resins, supported mineral acids, and zeolites has attracted much attention (Dijs et al., 2002; Fang et al., 2006). However, most solid acid catalysts have disadvantages related to high mass transfer resistance, product selectivity, and the tendency to deactivation in practical application of the esterification process.

Ionic liquids with excellent thermal stability, negligible volatility, and a variety of structures are recognized as an alternative of conventional catalysts and they have been extensively studied in the field of organic reactions, especially esterification (Wasserscheid & Keim, 2000; Visser et al., 2001; Chowdhury et al., 2007). The application of ionic liquids, including alkane sulfonic acid IL used in the temperaturecontrolled liquid-solid separation system (Bates et al., 2002), double SO_3H -functionalized ILs (Zhang et al., 2007), protonated N-alkylimidazolium ILs (Zhi et al., 2009), and ILs with acidic counter anions (Liu et al., 2011) for esterification has been reported. IL catalysts were also reported for the butyl butyrate synthesis using N-methylimidazole and 1,3-propane sultone (Han & Zhou, 2011). Unfortunately, the use of ionic liquids to prepare catalysts leads to long reaction times, large reaction volume, high viscosity of the catalyst (Sahoo et al., 2009; Zhu et al., 2009). Recently, polymer supported catalysts were developed for esterification reactions. Specifically, a novel Brønsted acidic heteropolyanion-based polymeric hybrid catalyst was synthesized and applied to various esterification processes (Leng et al., 2008). However, the preparation of this kind of catalyst has some disadvantages such as complex preparation and high cost.

Polyvinylpolypyrrolidone (PVPP) is usually used as an adsorbent to remove haze-active polyphenols from beer and wine by forming hydrogen bonds or

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[PVPP-BS]HSO4

Fig. 1. Preparation of polymeric IL [PVPP-BS]HSO₄.

Van der Waals interactions (Laborde et al., 2006). Because of its nontoxicity, hydrophilicity, and insolubility, PVPP is gaining considerable attention as a catalyst. Polyvinylpolypyrrolidone-supported boron trifluoride has been studied for the synthesis of 1,8-dioxooctahydroxanthenes and 1,8-dioxodecahydroacridines and the results indicated that the polyvinylpolypyrrolidone-supported boron trifluoride complex is a high loaded polymer supported Lewis acid, which is stable and retains its effective activity (Mokhtary & Langroudi, 2014). Consequently, this paper attempted to develop an efficient, environment friendly, low-cost polymeric acidic catalyst $([PVPP-BS]HSO_4)$ synthesized by coupling SO₃Hfunctionalized PVPP with H_2SO_4 for the synthesis of butyrate. In addition, the optimum conditions of butyric acid esterification with benzyl alcohol, as well as the catalytic activity and reusability of this catalyst are also discussed in this paper.

Experimental

Commercially available PVPP was purchased from Gobekie New Materials Science & Technology Co. (Shanghai, China). 1,4-Butane sultone (BS, 99 %) and sulfuric acid (AR grade) were purchased from Aladdin (Shanghai, China). FT-IR spectra measurements were performed on a PRESTIGE-21 FT-IR absorption spectrometer using KBr in the 4000– 400 cm⁻¹ region. Thermal decomposition point was obtained by TGA Q50 (New Castle, DE, USA) at the heating rate of $10 \,^{\circ}$ C min⁻¹ under nitrogen atmosphere. Elemental analyses and surface morphologies of [PVPP-BS]HSO₄, PVPP-BS and PVPP were investigated by a Hitachi SU8000 (Tokyo, Japan) field emission scanning electron microscope (FESEM). The BET surface area was measured at the liquid-nitrogen temperature using a Micromeritics SSA4200 analyzer (Beijing, China). The samples were degassed at 100 °C to the vacuum of 0.13 Pa before the BET surface area analysis. The acid value of [PVPP-BS]HSO₄ was determined by acid–base titration (Kafuku et al., 2010; Shah et al., 2014).

PVPP-BS and [PVPP-BS]HSO₄ were prepared according to the following procedure. In a 250 mL roundbottomed flask, BS (6 g) was added to PVPP (10 g) dispersed in toluene and the resulting mixture was slowly stirred and heated to 80 °C for about 24 h. Upon completion, the mixture was cooled down to the room temperature and filtrated. After filtration, the zwitterion (PVPP-BS) was washed with ethyl acetate three times and dried in vacuum at 60 °C.

The obtained PVPP-BS was dispersed first in methanol; then, sulfuric acid (4.32 g, 2.4 mL) in equimolar amount to BS was added to the mixture at 0 °C and stirred for 24 h. On completion, the mixture was washed three times with methanol to remove nonionic residues. Then, methanol was removed from the mixture in vacuum at 60 °C and the final product [PVPP-BS]HSO₄ was obtained. The preparation process is shown in Fig. 1.

Typical butyric acid esterification with benzyl al-



Fig. 2. Comparative FT-IR spectra of PVPP (a), PVPP-BS (b), [PVPP-BS]HSO4 (c), and H₂SO₄ (d).

cohol was conducted as follows: butyric acid (7.0488 g), benzyl alcohol (10.3814 g), cyclohexane (8 mL, as a water-carrying agent), and catalyst [PVPP-BS]HSO₄ (1.394 g) were put in a three-necked flask equipped with a thermometer and a water segregator with a reflux condenser. The resulting mixture was stirred at 90 °C in an oil bath for 3 h. Upon completion, the reaction mixture was cooled to room temperature and the obtained ester was separated from the mixture.

Chemical analysis of the products was done using a gas chromatograph Agilent 7890A GC (Palo Alto, CA, USA) with an HP 5 capillary column (30 m \times 0.32 mm \times 0.25 µm) and an FID detector. The butyrate yield was calculated from the concentration of butyrate as described in literature (Liang, 2013; Wang et al., 2008).

In the recycling tests, the catalyst [PVPP-BS] HSO_4 was reused after being heated in vacuum at 60 °C for 2 h. The recovered catalyst was directly used in the next run.

Results and discussion

Characterization of [PVPP-BS]HSO₄

A comparison of the FT-IR spectra recorded for PVPP, PVPP-BS, [PVPP-BS]HSO₄, and H₂SO₄ is presented in Fig. 2; three characteristic peaks at 1290 cm⁻¹ (C—N), 1438 cm⁻¹ (C—C), 1654 cm⁻¹ (C=O) can be observed in the PVPP spectrum (Fahmy et al., 2009). As for PVPP-BS (Fig. 2; curve b), the band at 1035 cm⁻¹ was assigned to the S=O symmetric stretching vibrations of the -SO₃H group. For H₂SO₄, the symmetric stretching vibration of the S=O band was shifted from 610 cm⁻¹ to 617 cm⁻¹ compared with that in the [PVPP-BS]HSO₄ spectrum. This result indicates that



Fig. 3. TGA patterns of PVPP (a), PVPP-BS (b), and $[PVPP-BS]HSO_4$ (c).

polymeric cations and HSO_4^- are combined by strong ionic interactions and that a PVPP-based polymeric hybrid was produced through the combination of SO₃H-functionalized PVPP with H₂SO₄ via ionic linkages.

Thermal analysis of PVPP, PVPP-BS, [PVPP-BS] HSO₄ achieved by TG is presented in Fig. 3; thermal decomposition temperature of PVPP was observed to be about 350 °C. Also, the drastic mass loss of PVPP-BS and [PVPP-BS]HSO₄ in Fig. 3 (curves b and c) in the temperature range of 350–500 °C corresponds to the thermal decomposition of PVPP in the catalyst. In Fig. 3 (curve b), an approximately 4.5 % mass loss of PVPP-BS was observed between 150 °C and 190 °C, and an approximately 3 % mass loss of [PVPP-BS]HSO₄ occurred between 200 °C and 240 °C (curve c). The results indicate lower decomposition temperature and higher mass loss of PVPP-BS compared to [PVPP-BS]HSO₄, thus H₂SO₄ is immobilized on PVPP-BS as a ionic hybrid.

Fig. 4 presents the results of field emission scanning electron microscopy (FESEM) of PVPP, PVPP-BS, and [PVPP-BS]HSO₄. In Fig. 4a, amorphous PVPP particles with the diameter of $3-5 \ \mu m$ were aggregated together. After the reaction with BS or H_2SO_4 , the surface morphology of PVPP-BS (Fig. 4b) or $[PVPP-BS]HSO_4$ (Fig. 4c) changed and was not as smooth as that of PVPP; also, small particles appeared on the surface of PVPP in both cases. Specifically, the BET surface area of PVPP-BS and [PVPP-BS]HSO₄ was much higher than that of PVPP (see Table 1). Moreover, the results of relative element content in PVPP-BS and [PVPP-BS]HSO₄ (see Table 1) showed that the content of sulfur increased in [PVPP-BS]HSO₄. All these findings demonstrate that BS and H_2SO_4 had already reacted with PVPP.

S. Wang et al./Chemical Papers 70 (5) 538-544 (2016)



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Fig. 4	. SEM	images	of PVPP	(a),	PVPP-BS	(b), and	[PVPP-BS]HSO ₄	(c)).
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Table 1	1.	Characterization	data	\mathbf{of}	PVPP,	PVPI	P-BS,	and	[PVP	P-BS]HSO	4
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Concela	$Acidity^a$	Acidity ^a BET surface area		$w_{ m i}{}^b/{ m mass}~\%$					
Sample	${ m mg~g^{-1}}$	$\mathrm{m}^2~\mathrm{g}^{-1}$	S	Ο	Ν	С			
PVPP	_	3.84	_	11.33	12.14	76.53			
PVPP-BS	-	6.28	0.27	18.61	17.59	63.53			
$[PVPP-BS]HSO_4$	274.89	6.56	0.42	25.72	22.91	50.95			

a) Determined as KOH mass consumed for neutralization; b) relative element mass percentage obtained by elemental analysis using FESEM.

Effect of reaction conditions on esterification

Fig. 5 shows the influence of the mole ratio of benzyl alcohol to butyric acid on the yield of benzyl butyrate; the mole ratio of benzyl alcohol to butyric acid varied from 1 : 1 to 1.5 : 1 with excessive addition of the reactant, benzyl alcohol, to increase the yield of benzyl butyrate. Due to the different mass ratios of benzyl alcohol to butyric acid, the yield of benzyl butyrate varied from 94 % to approximately 97 %. The highest yield of benzyl butyrate obtained was 96.8 % at the benzyl alcohol to butyric acid at mole ratio of 1.2 : 1 within 4 h. However, further increase of the benzyl alcohol to butyric acid mole ratio did not increase the yield of benzyl butyrate. This result is in a good agreement with the literature that the excess benzyl alcohol dissolves [PVPP-BS]HSO₄ (Huang et al., 2007; Han & Zhou, 2011). Thus, the optimum mole ratio of BS to PVPP was chosen to be 1.2 : 1 in this experiment.



Fig. 5. Yield of benzyl butyrate at different mole ratios of reactants (reaction conditions: [PVPP-BS]HSO₄ (8 mass %), 130 °C, 4 h).



Fig. 6. Yield of benzyl butyrate using different amounts of the catalyst (reaction conditions: benzyl alcohol (96 mmol), butyric acid (80 mmol), 130 °C, 4 h).

Influence of the amount of $[PVPP-BS]HSO_4$ on the yield of benzyl butyrate is presented in Fig. 6; the yield of benzyl butyrate changed with the increase in the amount of $[PVPP-BS]HSO_4$ and a 96.8 % yield of benzyl butyrate was obtained in the presence of 8 mass % of [PVPP-BS]HSO₄ within 4 h of the reaction. However, when the amount of the catalyst exceeded 8 mass %, the yield of benzyl butyrate decreased slightly probably due to the solubility of the catalyst in benzyl alcohol and its low solubility in benzyl butyrate. Solubility of the catalyst was also restricted by the degree of ester and benzyl alcohol mixing. Similar results were reported by other authors (Huang et al., 2007; Han & Zhou, 2011). Thus, the optimum catalyst amount of [PVPP-BS]HSO₄ used in this reaction was 8 mass %.

Fig. 7 depicts the changes of benzyl butyrate yield at different temperatures. The results indicate that



Fig. 7. Yield of benzyl butyrate at different temperatures (reaction conditions: benzyl alcohol (96 mmol), butyric acid (80 mmol), [PVPP-BS]HSO₄ (8 mass %), 4 h).



Fig. 8. Yield of benzyl butyrate at different reaction times (reaction conditions: benzyl alcohol (96 mmol), butyric acid (80 mmol), [PVPP-BS]HSO₄ (8 mass %), 130 °C).

the yield of benzyl butyrate changed with the temperature increase from $115 \,^{\circ}$ C to $135 \,^{\circ}$ C reaching 96.8 % at $130 \,^{\circ}$ C. However, at the reaction temperatures above $130 \,^{\circ}$ C, the benzyl butyrate yield did not increase further. Therefore, the optimum reaction temperature for this reaction was $130 \,^{\circ}$ C.

The effect of reaction time on the benzyl butyrate yield is shown in Fig. 8. It is evident that the reaction yield increased with the reaction time increase from 1 h to 4 h reaching 96.8 % after 4 h. However, when the reaction time exceeded 4 h, the yield of benzyl butyrate decreased slightly. Therefore, the optimum reaction time of 4 h was selected for this experiment.

Catalytic activities and reusability of different catalysts

Catalytic performance of different catalysts in the

Table 2. Esterification of butyric acid and benzyl alcohol with
 different catalysts^a

Entry	Catalyst	Phenomenon	$\mathrm{Yield}^b/\%$
1	_	Homogeneous	37.5
2	H_2SO_4	Homogeneous	85.5
3	p-CH ₃ C ₆ H ₄ SO ₃ H	Homogeneous	89.2
4	$[PVPP-BS]HSO_4$	Liquid-solid	96.8

a) Esterification conditions: benzyl alcohol (96 mmol), butyric acid (80 mmol), 130 °C, 4 h, [PVPP-BS]HSO₄ (1.39 g) or H₂SO₄ (0.34 g, with a similar proton content as [PVPP-BS]HSO₄) or p-CH₃C₆H₄SO₃H (1.19 g, with a similar proton content as [PVPP-BS]HSO₄); b) yield of butyrate based on the results of GC analysis.

butyric acid esterification with benzyl alcohol is provided in Table 2. According to the data, it can be concluded that the benzyl butyrate yield reaches just 37.5 % without using catalysts, which indicates that the esterification reaction is difficult to proceed without catalysts. When H_2SO_4 and $p-CH_3C_6H_4SO_3H$ participated in the esterification reaction as catalysts, the unsatisfying yield of 85.5 % and 81.9 %, respectively, was achieved. Also, the homogeneous reaction system complicates the separation of these catalysts. In contrast, [PVPP-BS]HSO₄ as a catalyst participating in the esterification reaction showed a high yield of 96.8 %. Moreover, this catalyst can be easily separated by vacuum filtration from the liquid-solid reaction system. These contradictory results indicate that [PVPP-BS]HSO₄ has more advantages than the other two catalysts studied.

Recycling of [PVPP-BS]HSO₄ after the butyric acid esterification with benzyl alcohol is illustrated in Fig. 9; [PVPP-BS]HSO₄ was recycled and reused in six runs. In the first run, the yield of benzyl butyrate reached 96.8 %, while it slightly decreased to 91.2 % in the sixth run. During the six runs, only a slight decrease in its catalytic activity was observed, which can be ascribed to the loss of HSO_4^- ions as reported in literature (Miao et al., 2011).

Butyric acid and different alcohols as the reactants were also tested using $[PVPP-BS]HSO_4$ as the catalyst to clarify the scope and limitations of this cat-



Fig. 9. Reusability of $[PVPP-BS]HSO_4$ in the synthesis of benzyl butyrate.

alyst in the esterification reaction. Table 3 presents the results of butyric acid esterification with different alcohols catalyzed by $[PVPP-BS]HSO_4$. It is evident that $[PVPP-BS]HSO_4$ possesses high catalytic activity for the esterification of butyrate providing yields of above 90 % in all investigated reactions. Therefore, $[PVPP-BS]HSO_4$ can be applied to various esterification reactions as a catalyst.

Conclusions

A new heterogeneous catalyst based on polyvinylpolypyrrolidone was prepared, and the experiments showed that the optimum reaction conditions of butyric acid esterification with benzyl alcohol are the butyric acid to benzyl alcohol mole ratio of 1 : 1.2, reaction temperature of $130 \,^{\circ}$ C, reaction time of 4 h and the amount of catalyst of 8 mass %. Under the optimized conditions, the yield of benzyl butyrate reached 96.8 %. Reusability of the [PVPP-BS]HSO₄ catalyst was also studied in this work, excellent stability and catalytic activity of the [PVPP-BS]HSO₄ catalyst has been proved, as it can be reused six times without noticeable decrease of its catalytic activity. Moreover, this catalyst can be efficiently applied in the butyric acid reactions with other alcohols and the yield of bu-

Table 3. Esterification of butyric acid with different alcohols in the presence of $[PVPP-BS]HSO_4^a$

$\mathrm{Yield}^b/\%$	
96.9	
90.8	
91.6	
93.4	
93.8	

a) Alcohol (96 mmol), carboxylic acid (80 mmol), [PVPP-BS]HSO₄ (8 mass %), 3 h; b) yield of butyrate based on the results of GC analysis.

tyrate can be maintained at above 90 %. Thus, the polymeric ionic liquid catalyst $[PVPP-BS]HSO_4$ is an attractive candidate for industrial butyrate synthesis.

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