

Research Article

Polyvinylpolypyrrolidone Supported Brønsted Acidic Catalyst for Esterification

Song Wang and Chengcheng Tian

School of Science, Shenyang University of Technology, Shenyang 110870, China

Correspondence should be addressed to Song Wang; 1259669134@qq.com

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A polyvinylpolypyrrolidone (PVPP) supported Brønsted acidic catalyst ([PVPP-BS]HSO₄) was prepared by coupling SO₃H-functionalized polyvinylpolypyrrolidone with H₂SO₄ in this work. After the characterization through FT-IR, FESEM, TG, BET, and elemental analysis, it was found that 1,4-butane sultone (BS) and sulfuric acid reacted with PVPP and were immobilized on PVPP surface. The prepared [PVPP-BS]HSO₄ catalyst shows high catalytic activity for a series of esterification reactions and could be separated from the reacted mixture easily. Moreover, this catalyst could be recycled and reused for six times without significant loss of catalytic performance.

1. Introduction

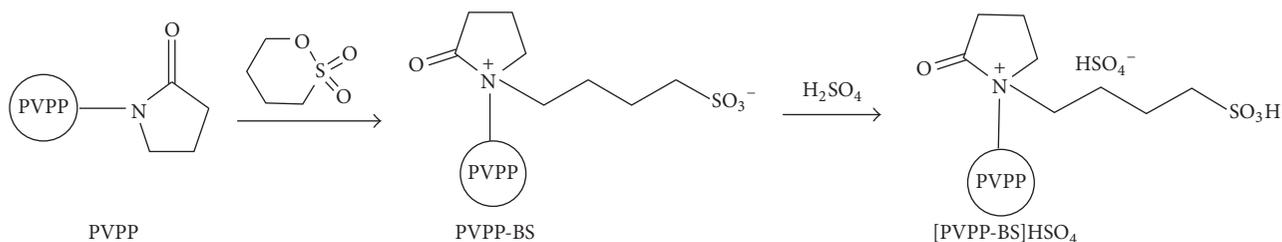
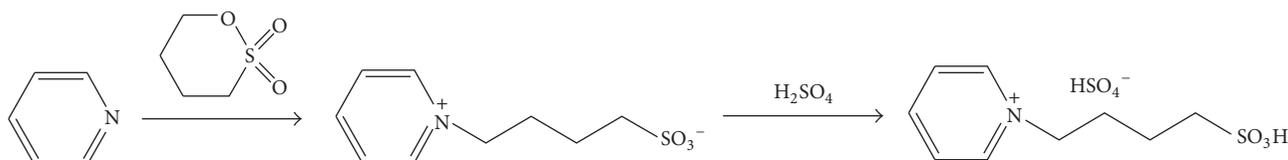
Esters have been widely used as lubricating oils, perfumes, plasticizers, biodegradable materials, and so forth [1, 2]. Conventionally, esterification could be catalyzed by mineral acids such as H₂SO₄ and H₃PO₄. However, these acids were reported to exhibit several drawbacks including severe corrosion to equipment, environmental hazards, and difficulty in the aspect of catalyst reusability [3]. To overcome these problems, heterogeneous solid acid catalysts such as supported mineral acids, acidic resins, and zeolites were developed [4]. Nevertheless, these heterogeneous catalysts were illustrated to exhibit some disadvantages related to product selectivity, catalyst recyclability, and environmental safety [5]. As such, developing high catalytic activity, recyclable, environmental-friendly catalysts for esterification is still an attractive topic in catalyst field [6].

Owing to the negligible selective dissolvability and tunable acidity, ILs (ionic liquids) were utilized as environmental-friendly solvents and catalysts for chemical reactions [7–10]. Many organic reactions were catalyzed by ILs which were revealed to be promising catalysts for esterification and transesterification. Gui et al. [11] employed three halogen-free Brønsted acidic ionic liquids as catalysts for esterification

of ethanol with acetic acid. They illustrated that these ILs were effective catalysts for esterification with the conversion rate of ethanol higher than 92%. Nevertheless, ILs were demonstrated to have some disadvantages such as high viscosity, inconvenient reusability, and large amount needed in reaction [12, 13].

In recent years, polymer supported catalysts were developed, which had advantages in product purification, reducing environmental damage, and easy separation from product. These exhibited characteristics made polymer supported catalysts promising for both academic and industrial applications [14–17]. Leng et al. [18] prepared a polymer supported acidic catalyst by coupling a polymeric IL with heteropolyanions, and their findings showed that when this catalyst was used in the esterification of acetic acid with n-butanol, a conversion rate of n-butanol higher than 97% was obtained. However, due to the complex preparation and polymerization of the monomer, the whole preparation process of polymer supported acidic catalysts is always complicate and less satisfactory.

Polyvinylpolypyrrolidone [PVPP] is a commercial product usually used as adsorbent [19, 20]. Recently, its application in catalyst field has drawn much attention because it has many advantages such as being insoluble in all kinds of solvents

SCHEME 1: Synthesis of [PVPP-BS]HSO₄.SCHEME 2: Synthesis of [BSPy]HSO₄.

and nontoxic. Mokhtary and Najafzadeh [21] used PVPP supported boron trifluoride as the catalyst to prepare *N-tert*-butyl amides by reaction of nitriles with *tert*-butyl acetate. They found that PVPP supported boron trifluoride was a high efficient Lewis acid. In this study, a commercial PVPP was applied to synthesize a Brønsted acidic catalyst. The catalytic activity and reusability performance of this catalyst used for esterification reactions were also investigated.

2. Experimental Part

2.1. Materials. PVPP was provided by Gobekie New Materials Science & Technology Co., Ltd, Shanghai, China. 1,4-Butane sultone (BS) (99%), sulfuric acid (98%), and other chemicals (AR grade) were purchased from Sinopharm Chemical Reagent Co. and used as received.

2.2. Preparation of [PVPP-BS]HSO₄, PVPP-H₂SO₄, and 1-(4-Sulfonic acid) Butylpyridinium Hydrogen Sulfate ([BSPy]HSO₄). All experimental steps were carried out under nitrogen atmosphere. First, [PVPP-BS]HSO₄ was prepared in the following steps. Under vigorous stirring, PVPP powder (10 g, monomer molar quantity was about 0.09 mol) was dispersed in toluene and then an appropriate amount of BS (ranging from 0 to 0.09 mol) was added to the mixture. The mixture was slowly heated to 80°C and continuously stirred in a 250 mL round-bottomed flask for 24 h. After filtration, the zwitterions powder (PVPP-BS) was washed three times with ethyl acetate and then dried in vacuum at 60°C to obtain PVPP-BS. Then, sulfuric acid (ranging from 0 to 0.09 mol) in equimolar amount to BS was added to the mixture of PVPP-BS dispersed in methanol at 0°C and stirred for 24 h. On completion, the mixture was filtered and washed three times with methanol, and then water and methanol were removed in vacuum at 60°C to afford the final product [PVPP-BS]HSO₄ as a solid. The preparation process of [PVPP-BS]HSO₄ is shown in Scheme 1.

For comparison, two other catalysts PVPP-H₂SO₄ and 1-(4-sulfonic acid) butylpyridinium hydrogen sulfate

([BSPy]HSO₄) were also prepared. The preparation procedure of PVPP-H₂SO₄ was as follows. PVPP powder (10 g) was dispersed in ethyl acetate and then sulfuric acid (0.09 mol) was added to the mixture at 0°C and stirred for 24 h. On completion, the mixture was filtered and washed three times with methanol. Then, water and methanol were removed in vacuum at 60°C to afford the final product of PVPP-H₂SO₄ as a solid.

[BSPy]HSO₄ was synthesized as reported in the previous literature with a slight modification [22]. Pyridine (0.11 mol) and 1,4-butane sultone (0.1 mol) were introduced into a 100 mL capacity round-bottom flask reactor equipped with a reflux condenser, a magnetic stirrer, and a thermometer. This reaction system was stirred magnetically under reflux at 40°C for 24 h until a white solid zwitterion (BSPy) formed, which was filtered, washed with ethyl acetate three times to remove nonionic residues, and dried in vacuum. Sulfuric acid (0.1 mol) was added dropwise and the mixture was stirred at 80°C for 8 h. The obtained viscous liquid was washed with ether for three times and dried in vacuum to form ionic liquid [BSPy]HSO₄. The preparation process of [BSPy]HSO₄ is shown in Scheme 2.

2.3. Catalyst Characterization. FT-IR spectra were measured on a PRESTIGE-21 FT-IR instrument (KBr discs) in the 2200–400 cm⁻¹ region. Thermal analysis was performed with a TA Q50 thermogravimetric analyzer in a nitrogen atmosphere with a heating rate of 10°C/min. The surface morphologies of PVPP, PVPP-BS, and [PVPP-BS]HSO₄ were investigated by using a Hitachi SU8000 field emission scanning electron microscopy (FESEM). Elemental analysis was performed on an Elementar Vario EL Cube elemental analyzer. The BET surface area was measured at the liquid-nitrogen temperature using a Micromeritics SSA4200 analyzer. Before the BET surface area analysis, the samples were degassed at 100°C to the vacuum of 0.13 Pa. The multipoint Brunauer-Emmett-Teller (BET) method was used to measure total surface area. The acid value of [PVPP-BS]HSO₄ was determined by acid-base titration [23, 24]. One-half gram of

the catalyst powder was dispersed in 50 mL of 0.1 M KCl. The dispersion was stirred for 20 min and titrated with 0.1 M KOH in the presence of phenolphthalein.

2.4. Esterification and Analysis. Taking the esterification of acetic acid with n-butanol as an example, the typical reaction was carried out as follows: acetic acid (0.08 mol), n-butanol (0.096 mol), cyclohexane (8 mL, as a water-carrying agent), and [PVPP-BS]HSO₄ (1.19 g, 8% of the total mass of n-butanol and acetic acid) were introduced into a 100 mL capacity round-bottom flask reactor equipped with a water segregator, thermometer, reflux condenser, and magnetic stirrer. The mixture was heated under reflux at 90°C with vigorous stirring for 3 h. After the reaction completed, the product was analyzed by a gas chromatograph (GC) instrument with FID detector (Agilent 7890 A, HP 5 capillary column 30 m × 0.32 mm × 0.25 μm). Other esterification reactions were carried out in the same procedure. The conversion of the carboxylic acid and the selectivity of esters were determined as described in previous literatures [18, 25].

2.5. Recycling of Catalysts. The catalyst [PVPP-BS]HSO₄ was recovered by vacuum filtration and dried in vacuum at 60°C for 2 h. This recovered catalyst was directly used for the next run.

3. Results and Discussion

3.1. Effect of the Ratio of BS to the Pyrrolidone Repeat Unit of PVPP on the Catalytic Activity. BS can only react with the pyrrolidone repeat unit exposed on the surface of PVPP because PVPP is a cross-linking insoluble material. However, due to the lack of reliable method to measure the amount of the pyrrolidone repeat unit exposed on the surface of PVPP, the ratio of BS to the pyrrolidone repeat unit of PVPP, which can greatly affect the catalytic performance of the catalyst, cannot be calculated directly. Therefore, to examine the effect of the ratio of BS to the pyrrolidone repeat unit of PVPP on the catalytic activity, several catalysts synthesized with different mole ratio of BS to the pyrrolidone repeat unit of PVPP were utilized in the esterification of n-butanol with acetic acid. As shown in Figure 1, with the increase of mole ratio of BS to the pyrrolidone repeat unit of PVPP, a higher conversion rate of acetic acid was obtained. When the mole ratio of BS to the pyrrolidone repeat unit of PVPP was increased up to 0.5, the achieved conversion of acetic acid was about 99.6%. With the mole ratio of BS to the pyrrolidone repeat unit of PVPP increased continually, the conversion did not change significantly. This result indicates that the satisfied ratio of BS to the pyrrolidone repeat unit of PVPP is 0.5.

3.2. Catalyst Characterization

3.2.1. FT-IR Spectroscopy. The FT-IR spectra results of PVPP, PVPP-BS, [PVPP-BS]HSO₄, and H₂SO₄ are presented in Figure 2. The characteristic peaks around 1290 cm⁻¹, 1438 cm⁻¹, and 1654 cm⁻¹ which could be clearly observed in Figure 2 were assigned to C-N, C-C, and C=O stretching

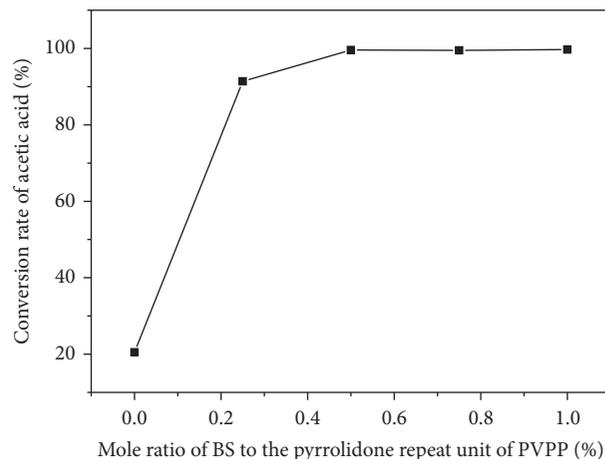


FIGURE 1: Conversion of acetic acid catalyzed by [PVPP-BS]HSO₄ catalysts synthesized with different mole ratios of BS to the pyrrolidone repeat unit of PVPP. (Reaction conditions: n-butanol 96 mmol, acetic acid 80 mmol, [PVPP-BS]HSO₄ catalyst 8 wt%, and 90°C for 3 h.)

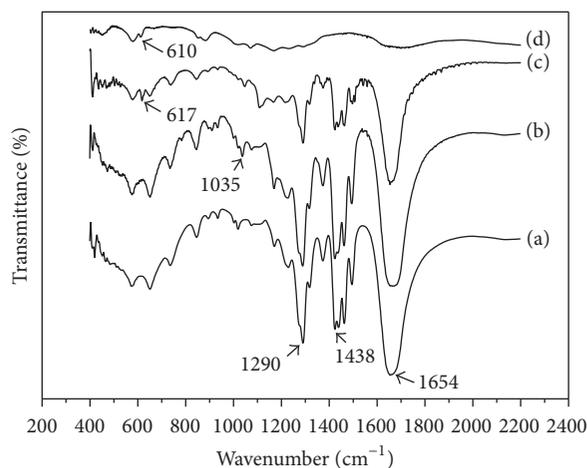


FIGURE 2: The comparative FT-IR spectra of (a) PVPP, (b) PVPP-BS, (c) [PVPP-BS]HSO₄, and (d) H₂SO₄.

vibrations of PVPP, respectively [26]. The band in Figure 2(b) at 1035 cm⁻¹, which did not appear in Figure 2(a), was attributed to the S=O symmetric stretching vibrations as reported in a literature [22]. This result indicates that BS has been connected to the surface of PVPP. Moreover, comparing H₂SO₄ with [PVPP-BS]HSO₄ in Figures 2(d) and 2(c), it can be clearly observed that after PVPP-BS reacted with H₂SO₄, the symmetric stretching vibration of S-O band had shifted from 610 cm⁻¹ to 617 cm⁻¹. This is a convincing evidence of the existence of the strong ionic interaction between the polymeric cations and HSO₄⁻. It thus suggests that the reaction of SO₃H-functionalized PVPP with H₂SO₄ produced a PVPP-based polymeric hybrid via ionic linkages.

3.2.2. Thermogravimetric Analysis. Thermal stabilities of PVPP, PVPP-BS, and [PVPP-BS]HSO₄ were determined by

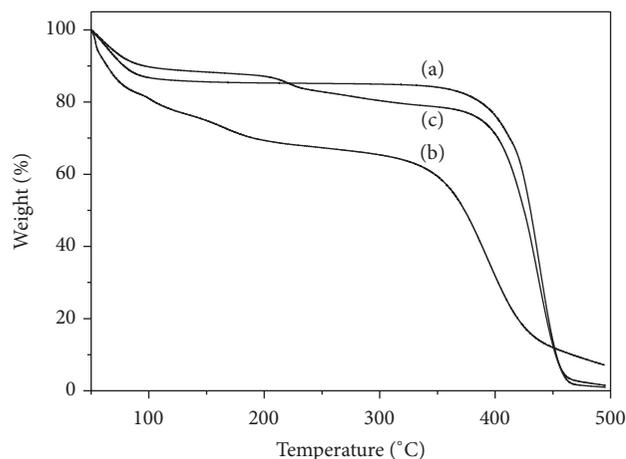


FIGURE 3: Thermogravimetric curves of (a) PVPP, (b) PVPP-BS, and (c) [PVPP-BS]HSO₄.

TG analysis. In Figures 3(b) and 3(c), besides the drastic weight loss at temperature ranging from 350°C to 500°C corresponding to the thermal decomposition of PVPP backbone in the catalyst, there was another weight loss around 200°C. The TG curve of PVPP-BS, curve (b) in Figure 3, shows that there was an approximately 4.5% weight loss of the sample between 150°C and 190°C, while that of [PVPP-BS]HSO₄, curve (c) in Figure 3, exhibits that there was an approximately 3% weight loss of the sample between 200°C and 240°C. The finding that [PVPP-BS]HSO₄ had much higher decomposition temperature and less weight loss than PVPP-BS strongly indicates that [PVPP-BS]HSO₄ is not a physical mixture of PVPP-BS with H₂SO₄ but an ionic hybrid.

3.2.3. Morphological Surface Analysis. Figure 4 shows the diameters and surface morphologies of (a) PVPP, (b) PVPP-BS, and (c) [PVPP-BS]HSO₄. It can be clearly seen that the amorphous PVPP particles before reaction were aggregated together with size of 3–5 μm (Figure 4(a)). However, after reacting with BS or H₂SO₄, the surface of PVPP-BS and [PVPP-BS]HSO₄ was not as smooth as that of PVPP, and small particles could be seen on the surface (Figures 4(b) and 4(c)). These small particles made the BET surface area of PVPP-BS (6.28 m²/g) and [PVPP-BS]HSO₄ (6.56 m²/g) much higher than that of PVPP (3.84 m²/g) (Table 1). The elemental analysis results in Table 1 demonstrate the difference in S element content in PVPP, PVPP-BS, and [PVPP-BS]HSO₄. The sulfur content in [PVPP-BS]HSO₄ (8.789%) was higher than that in PVPP-BS (4.121%). In contrast, no sulfur content was found in PVPP. These findings further demonstrate that BS and H₂SO₄ have already reacted with PVPP.

3.3. Catalytic Activities of Different Catalysts. The catalytic performance of different catalysts for the esterification of acetic acid with n-butanol is presented in Table 2. It can be observed that the conversion of acetic acid only reached 20.3% (entry 1) when catalysts were not used, which means

TABLE 1: Characterization data of PVPP, PVPP-BS, and [PVPP-BS]HSO₄.

Sample	S% ^a	Acidity ^b mg/g	BET surface area m ² /g
PVPP	–	–	3.84
PVPP-BS	4.121	–	6.28
[PVPP-BS]HSO ₄	8.789	274.89	6.56

^aWeight percentage of S element determined by an elemental analyzer

^bDetermined as KOH mass consumed for neutralization.

TABLE 2: Esterification of n-butanol and acetic acid under different conditions^a. CH₃COOH + CH₃(CH₂)₃OH → CH₃COO(CH₂)₃CH₃ + H₂O.

Entry	Catal.	Conv. (%) ^b	Sel. (%) ^c
1	–	20.3	100
2	H ₂ SO ₄	85.1	87.1
3	PVPP-H ₂ SO ₄	89.3	88.5
4	H ₃ PW ₁₂ O ₄₀	96.9	95.8
5	[BSPy]HSO ₄	96.1	100
6	[PVPP-BS]HSO ₄	99.6	100

^an-Butanol (7.12 g); acetic acid (4.80 g); and [PVPP-BS]HSO₄ (8 wt%), 90°C for 3 h. H₂SO₄, H₃PW₁₂O₄₀, PVPP-H₂SO₄, and [BSPy]HSO₄ were used in a similar proton content as [PVPP-BS]HSO₄.

^bConversion of acetic acid.

^cSelectivity for ester.

that the esterification was difficult to occur with the absence of catalysts. When H₂SO₄ was used as the catalyst in the esterification, a homogeneous reaction system was formed and H₂SO₄ exhibited a low conversion of 85.1% and selectivity of 87.1% (entry 2). This homogeneous reaction system made it difficult to separate H₂SO₄ from the product. Although PVPP-H₂SO₄ is a heterogeneous catalyst which is easy to prepare, when used as the catalyst in esterification, it exhibited the similar catalytic ability as H₂SO₄, and the low conversion of 89.3% and selectivity of 88.5% were obtained (entry 3). Using H₃PW₁₂O₄₀ as the catalyst in the esterification, it presented a relative high conversion of 96.9%. Nevertheless, due to its well-known strong acidity caused by the three protons in the cation position, H₃PW₁₂O₄₀ had a lower selectivity of reaction (95.8%) than that of [BSPy]HSO₄ and [PVPP-BS]HSO₄ (entry 4). When [BSPy]HSO₄ was used as the catalyst, a liquid-liquid reaction system was formed. The conversion of acetic acid was 96.1% which was much higher than that of H₂SO₄ and PVPP-H₂SO₄; and the selectivity of the reaction was 100%, which was higher than that of H₃PW₁₂O₄₀ (entry 5). However, [BSPy]HSO₄ was easily attached onto the bottom surface of the flask reactor like a gelatinous liquid, which greatly lowered the mass transfer. When [PVPP-BS]HSO₄ was used, a liquid-solid reaction system formed and a high conversion (99.6%) and good selectivity were obtained (entry 6). Moreover, [PVPP-BS]HSO₄ could be easily separated by vacuum filtration and reused.

Table 3 presents the comparison of the catalytic performances of [PVPP-BS]HSO₄ with two reported polymer

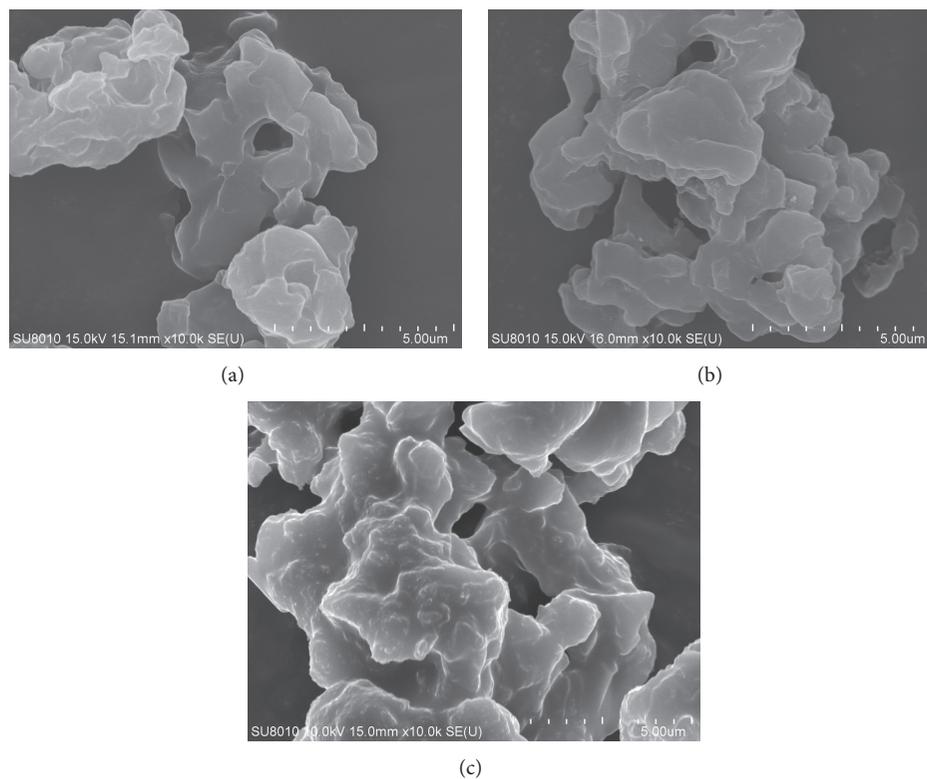


FIGURE 4: FESEM photographs of (a) PVPP, (b) PVPP-BS, and (c) [PVPP-BS]HSO₄.

TABLE 3: Esterification of n-butanol and acetic acid with different polymer supported catalysts.

Catalyst unit	Reaction conditions	Conv. (%) ^a
	n-Butanol 36 mmol, acetic acid 30 mmol, catalyst 4.5 wt%, 110°C for 1.5 h.	97.4 [18]
	n-Butanol 17 mmol, acetic acid 34 mmol, catalyst 9 wt%, 100°C for 6 h.	93.7 [27]
	n-Butanol 96 mmol, acetic acid 80 mmol, catalyst 5 wt%, 90°C for 3 h.	97.6

^aConversion of acetic acid.

TABLE 4: Esterification of different alcohols and carboxylic acids in [PVPP-BS]HSO₄^a.

Entry	Acids	Alcohols	Temp. (°C)	Conv. (%) ^b	Sel. (%) ^c
1	Acetic acid	n-Butanol	90	99.6	100
2	Acetic acid	n-Hexanol	92	99.1	100
3	Acetic acid	n-Octanol	92	95.4	100
4	Propionic acid	Isobutanol	91	99.3	100
5	n-Butyric acid	n-Butanol	94	93.8	100
6	Oleic acid	n-Butanol	92	95.6	100
7	Acetic acid	Benzyl alcohol	89	99.1	100
8	Propionic acid	Benzyl alcohol	90	93.2	100

^aAlcohol (96 mmol); carboxylic acid (80 mmol); and [PVPP-BS]HSO₄ (8 wt%), for 3 h.

^bConversion of acetic acid.

^cSelectivity for ester.

supported catalysts for the esterification of acetic acid with n-butanol. It can be seen that [PVPP-BS]HSO₄ exhibited similar catalytic performance as the two reported polymer supported catalysts. The conversion of acetic acid exceeded 90%, when these polymer supported catalysts were applied in esterification of n-butanol and acetic acid. However, the difference is that the polymer supports of the reported catalysts are in the stage of laboratory while the PVPP is a commercial product. Using PVPP as catalyst support can greatly simplify the preparation process and lower production costs of the catalyst in contrast to the other two catalysts reported by Leng et al. [18] and Li et al. [27]. Therefore, [PVPP-BS]HSO₄ has more potential in industrial application.

3.4. Catalytic Activity of [PVPP-BS]HSO₄ for Esterification of Other Alcohols and Carboxylic Acids. In order to clarify the scope and limitations of [PVPP-BS]HSO₄ catalyst for esterification, different alcohols and carboxylic acids as the reactants for esterification reactions were tested and the results are summarized in Table 4. It can be observed that [PVPP-BS]HSO₄ possessed very high catalytic activity for esterification. Excellent conversions above 90% with perfect selectivity (100%) for corresponding esters were obtained in all investigated reactions. Moreover, the results in Table 4 demonstrate that the length of carbon chains merely affected the conversion and the selectivity (Table 4, entries 1–6). In addition, satisfactory conversions above 90% (Table 4, entries 7, 8) of esterification of aromatic alcohol and carboxylic acids were also obtained. Thus, all these results indicate that [PVPP-BS]HSO₄ catalyst can be applied to various esterification reactions with different substrates.

3.5. Reusability of [PVPP-BS]HSO₄ for Esterification. Reusability of the catalyst is one of the essential aspects for practical applications. After the reaction of each run, the solid catalyst could be recovered by filtration, dried in vacuum at 60°C for 2 h. The recycling performance of [PVPP-BS]HSO₄ in the esterification of acetic acid with n-butanol is illustrated in Figure 5. The conversion of the acid changed from 99.6% to 96.5% after 5 times of recycling, which indicates the high catalytic performance of [PVPP-BS]HSO₄.

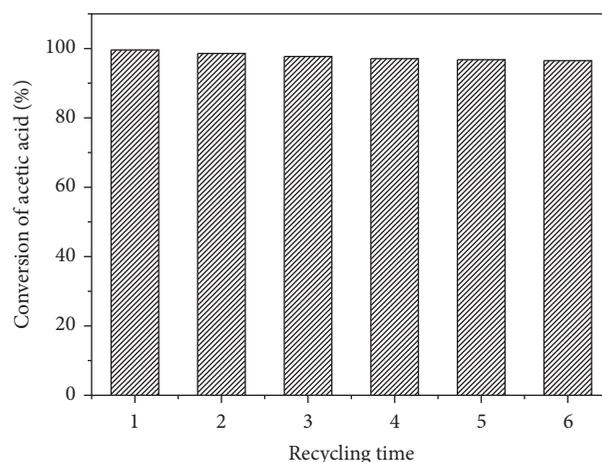


FIGURE 5: Recycling of [PVPP-BS]HSO₄ in the synthesis of n-butyl acetate.

4. Conclusions

In conclusion, a Brønsted acidic catalyst [PVPP-BS]HSO₄ was synthesized by coupling SO₃H-functionalized polyvinyl-pyrrolidone with H₂SO₄. This catalyst was revealed to be an efficient catalyst for various esterification reactions, presenting the advantages of practical convenience in product preparation, separation, and recovery. Moreover, the conversions for all the investigated reactions were above 90%. Conversions for the reactions could still be satisfactorily maintained above 90% after the catalyst was recycled for 5 times for the synthesis of n-butyl acetate. Thus, the [PVPP-BS]HSO₄ polymer supported catalyst, which was prepared in this study, was proved to be an efficient, reusable, and potential heterogeneous catalyst for the synthesis of carboxylic esters.

Competing Interests

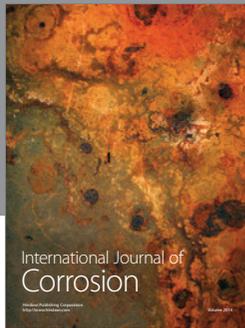
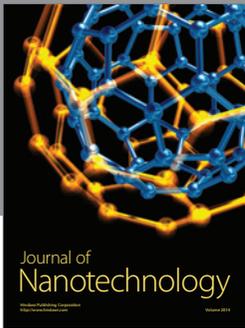
The authors declare that they have no competing interests.

Acknowledgments

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