

Supporting Information

Optimization of process variables in the synthesis of tributyl citrate using a polyvinylpolypyrrolidone supported Brønsted acidic ionic liquid catalyst

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Procedure of the elution experiment

The elution experiment was performed in the following procedure. First, about 1 g catalyst was weighted. Then the catalyst was washed three times with 20 mL of 0.1 M NaOH solution. After centrifugation separation, the catalyst was wash three times with 20 mL distilled water to ensure the elution of the IL on PVPP support. Finally, the solid residue was weighed after dried at 100 °C under vacuum overnight. Since the weight loss of the catalyst comes from the elution of the IL on the PVPP support, the weight loss percentage of the catalyst during the elution experiment is the same as the loading of the IL on the PVPP support. According to this elution experiment, the loading amount of the IL on the PVPP support is 3.9%.

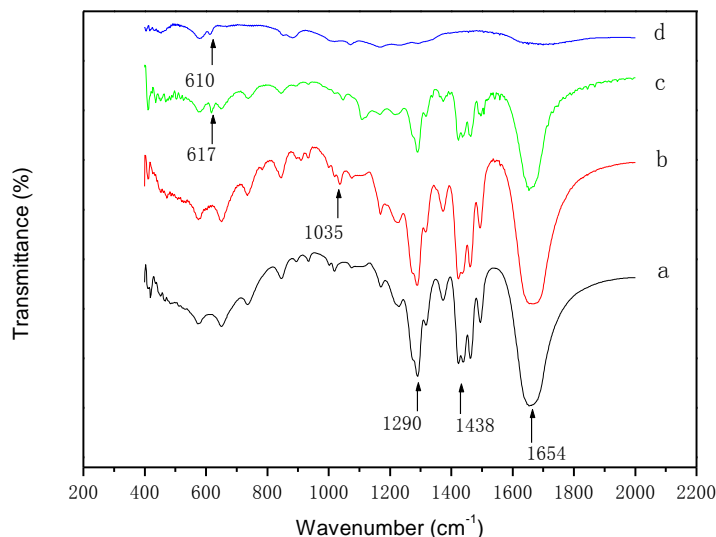


FIGURE S1: FT-IR spectra of a) PVPP, b) BsPVPP, c) [BsPVPP]HSO₄ and d) H₂SO₄.

Figure S1 shows the FT-IR spectra of a) PVPP, b) BsPVPP, c) [BsPVPP]HSO₄ and d) H₂SO₄. It can be observed in Figure S1a that three characteristic peaks appeared at about 1290 cm⁻¹, 1438 cm⁻¹, and 1654 cm⁻¹ corresponding to the C-N, C-C, and C=O stretching vibrations of PVPP. Compared with PVPP (Figure S1a), there was a new band appeared at 1035 cm⁻¹ which can be assigned to the S=O symmetric stretching vibrations of the SO₃ group in BsPVPP (Figure S1b). This observation demonstrates that BS has been loaded on the surface of PVPP. After BsPVPP reacted with H₂SO₄, by comparing Figure S1c and Figure S1d, it can be found that the symmetric stretching vibration of S-O group of H₂SO₄ had shifted from 610 cm⁻¹ to 617 cm⁻¹ which demonstrated that there was a strong ionic interaction between the polymeric support and HSO₄⁻ and the reaction of BsPVPP with H₂SO₄ lead to the formation of a PVPP-based polymeric ionic liquid compound.

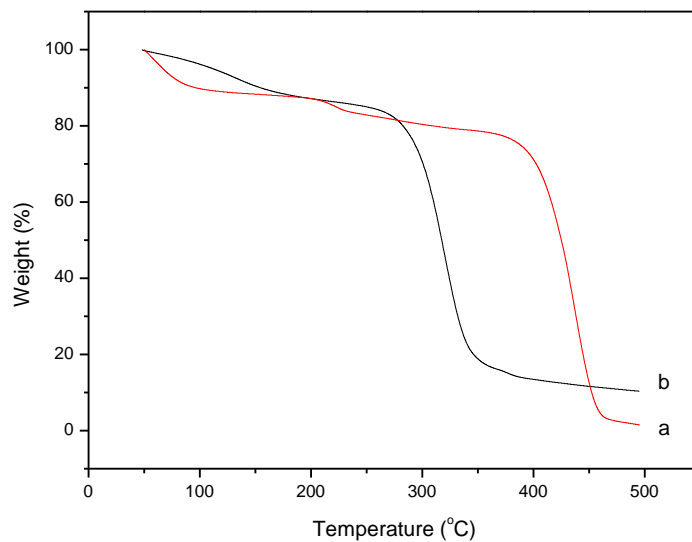
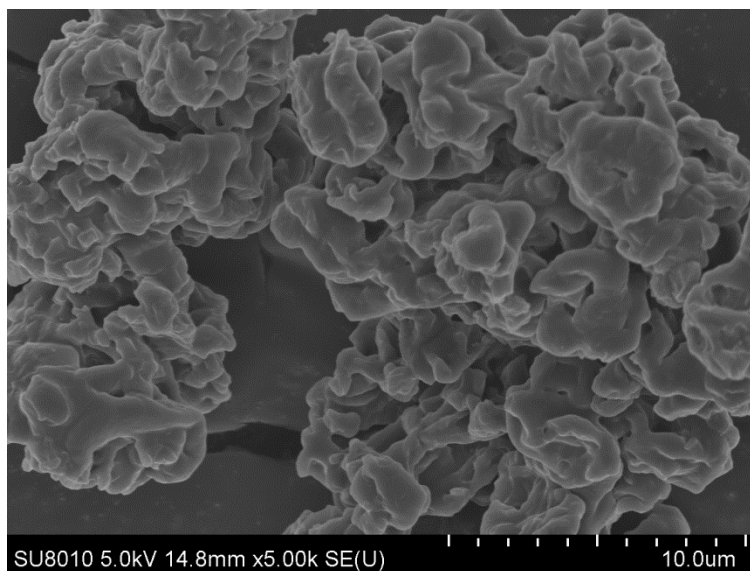


FIGURE S2: TGA curves of a) [BsPVPP]HSO₄ and b) [BsMIM]PTSA.

Figure S2 is the TGA curves of [BsPVPP]HSO₄ (a) and [BsMIM]PTSA (b). It can be observed that the thermal decomposition behavior of [BsPVPP]HSO₄ and [BsMIM]PTSA was different. [BsPVPP]HSO₄ had much better thermal stability than [BsMIM]PTSA because the thermal decomposition temperature for [BsPVPP]HSO₄ was in the range of 200°C -250°C and 350°C -450°C, which were all higher than that of [BsMIM]PTSA, 100°C -150°C and 250°C -350°C.

a



b

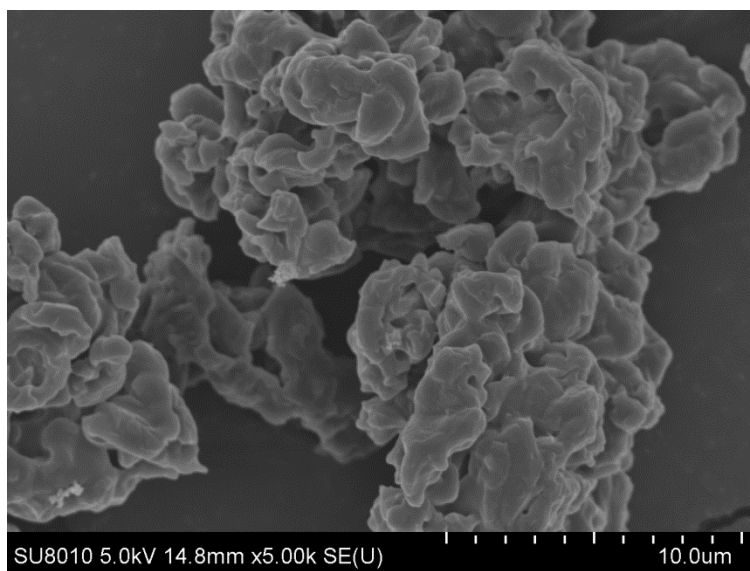


FIGURE S3: FESEM images of a) PVPP and b) [BsPVPP]HSO₄.

The morphology observation of the PVPP and [BsPVPP]HSO₄ indicated that the difference between the PVPP and [BsPVPP]HSO₄ was not remarkable. The only difference was that the surface of [BsPVPP]HSO₄ was not as smooth as PVPP, and small particles were observed on the surface of [BsPVPP]HSO₄.

T_{ABLE} S1: Energy-dispersive spectroscopy results of PVPP and [BsPVPP]HSO₄.

Sample	S(wt%)	O(wt%)	N(wt%)	C(wt%)
PVPP	—	11.33	12.14	76.53
[BsPVPP]HSO ₄	0.42	25.72	22.91	50.95

Table S1 shows the energy-dispersive spectroscopy results of PVPP and [BsPVPP]HSO₄. It can be observed that, after PVPP reacted with Bs and H₂SO₄, the content of S element in [BsPVPP]HSO₄ catalyst increased. This result indicated that the IL formed during the preparation process had been loaded on PVPP.

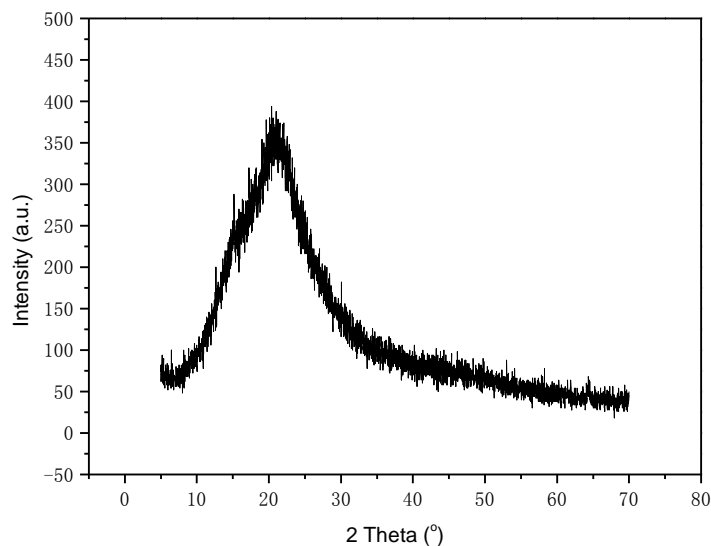


FIGURE S4: XRD result of [BsPVPP]HSO₄ catalyst

The XRD diffraction pattern of [BsPVPP]HSO₄ catalyst was depicted in Figure S4. No crystalline diffraction peak can be observed in the XRD profile which demonstrates that [BsPVPP]HSO₄ catalyst was amorphous at the room temperature (about 25°C). Because PVPP is a cross-linked polymeric material which can not crystallize, the XRD result also indicated that the IL supported on PVPP can not crystallize at the room temperature (about 25°C) and the IL supported on PVPP was a typical room temperature ionic liquid.

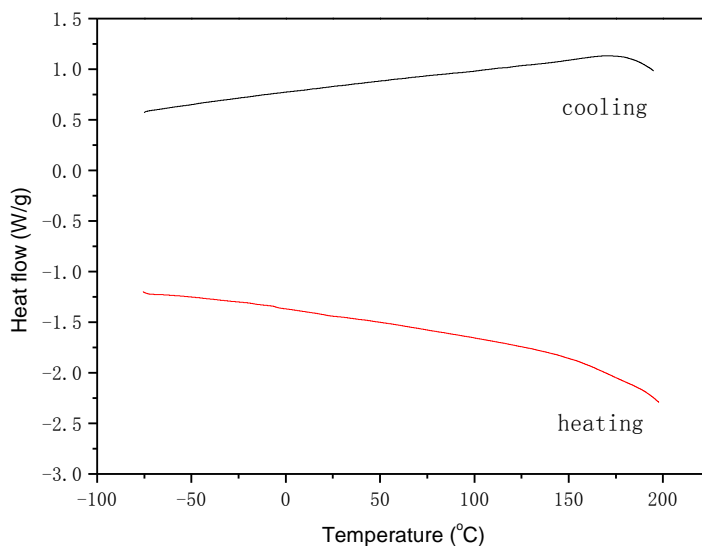


FIGURE S5: DSC result of [BsPVPP]HSO₄ catalyst

Figure S5 shows the DSC results of the [BsPVPP]HSO₄ catalyst. No obvious crystallization and melting peaks can be observed during the cooling and heating processes. This phenomenon was similar to the DSC investigation on 1-butyl-3-methylimidazolium hydrosulfate IL ([BuMeIm]HSO₄) [36]. During the DSC investigation on [BuMeIm]HSO₄ IL, the crystallization peak of [BuMeIm]HSO₄ can not be observed. And this feature was ascribed to the existence of strong hydrogen bonds inside the molecules caused by the interaction of cation with anion. Thus, this kind of similar phenomenon happened in the [BsPVPP]HSO₄ catalyst. Moreover, the content of IL loaded on PVPP was less than 4% (see elution experiment part), which can make it difficult to observe the crystallization behavior of [BsPVPP]HSO₄ catalyst clearly.

NMR result of [BsMIM]PTSA IL

^1H NMR (500 MHz, D_2O , ppm) : δ 1.73 (m, 2H) , 1.99 (m, 2H) , 2.38 (s, 3H) , 2.93 (t, 2H) , 3.87 (s, 3H) , 4.17 (t, 2H) , 7.35 (d, 1H) , 7.40 (s, 1H) , 7.45 (s, 1H) , 7.67 (d, 1H) , 8.69 (s, 1H) .

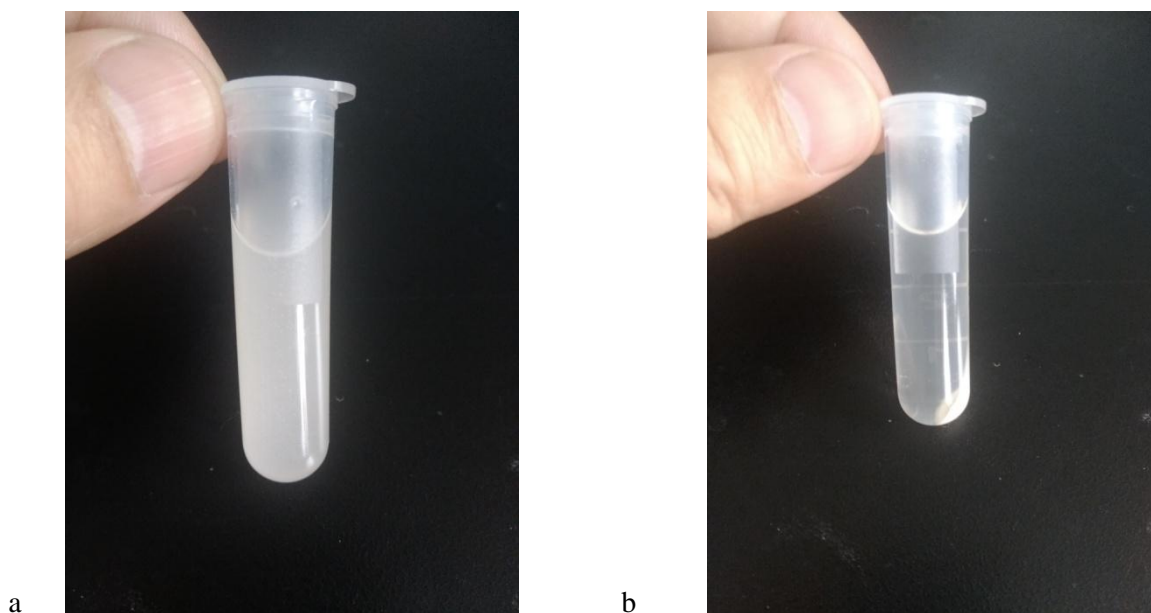
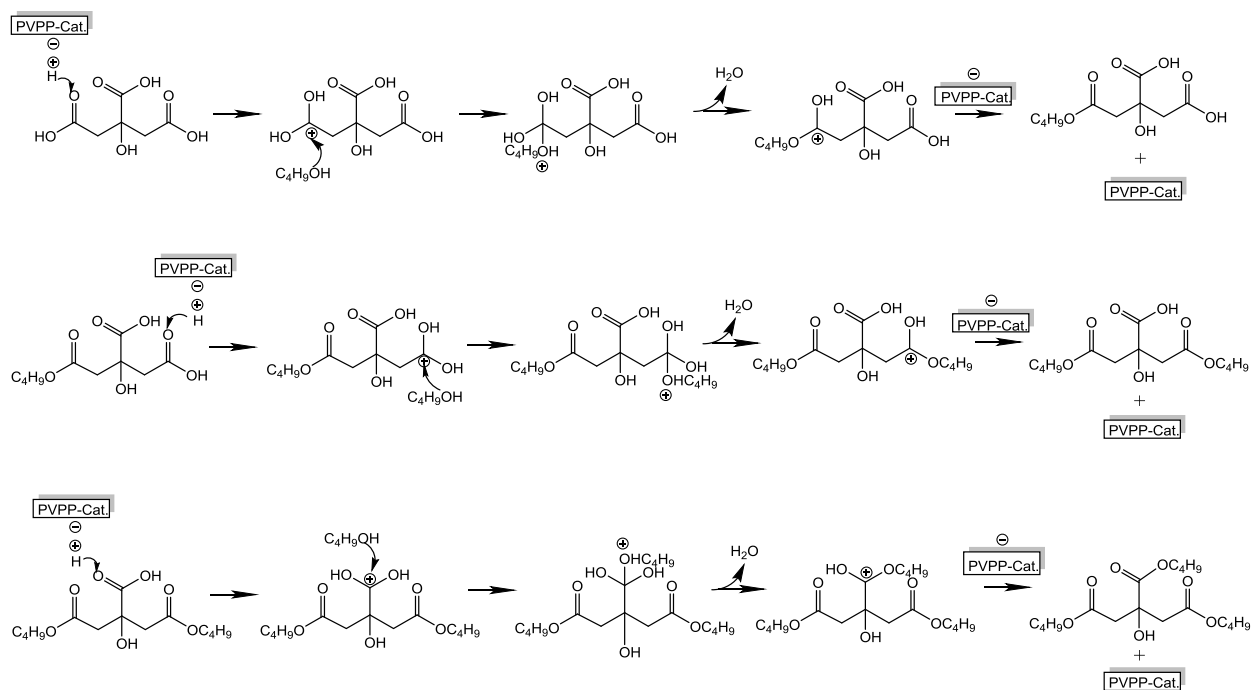


FIGURE S6: Conditions of the reaction system a) before and b) after centrifugation

It can be observed from Figure S6 that, before centrifugation, the product was turbid due to the suspension of the catalyst. After centrifugation, the product became clear and the catalyst gathered at the bottom of the tube. This result indicates that the catalyst is an easily separated and recyclable heterogeneous catalyst.



S_{HEME} S1: Proposed catalytic mechanism for esterification of citric acid with n-butanol over [BsPVPP]HSO₄ catalyst

[BsPVPP]HSO₄ catalyzed esterification of citric acid with n-butanol was based on the proton acid catalytic mechanism. In this classical mechanism, firstly, the carboxyl groups of reactant citric acid were activated by the hydrogen ions provided by the [BsPVPP]HSO₄ catalyst to form the carbonium ions, which can combine with the hydroxyl groups easily. Then after a hydrogen transfer and a dehydration process, an intermediate formed. Finally, the product butyl citrate was formed via a transfer process of hydrogen, which also led to the regeneration of the [BsPVPP]HSO₄ catalyst.