

Catalytic condensation of phenol with formaldehyde into BPF on recyclable anchoring sulfuric acid

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Abstract: A novel solid-acid catalyst (PVC-EDA-SO₄H) based on polyvinyl chloride (PVC) were prepared after amination of Ethylenediamine (EDA) and anchorage of sulfuric acid. The as-prepared catalyst was characterized by FT-IR, Element analysis, Chemical titration and Thermal analysis, the results indicated that the sulfuric acid was successfully anchored on PVC. The PVC-EDA-SO₄H showed excellent catalytic performance for the synthesis of bisphenol F, and achieved almost high yield and selectivity (94%) of BPF under the mild reaction conditions. Meanwhile, exhibited excellent reusability without the significant loss after six cycles via simple filtration.

1. Introduction

Bisphenol F[1-2] (BPF) as a high-quality chemical intermediate has been widely applied in fine chemical field including coatings, rubber and building structural rubbers. Typically, the synthesis of BPF is an acid-catalyzed condensation of phenol with formaldehyde. Therefore, development of acid catalyst for synthesis of BPF has drawn much attention in fine chemical fields. Traditionally, the homogeneous catalysts, such as liquid mineral acids (sulfuric acid, hydrochloric acid, phosphoric acid), are widely used to catalyzed the synthesis of BPF due to their low price and high active. However, the homogenous acid-catalyzed processes suffer from several significant drawbacks, such as harsh required equipment, troublesome purification and recovery problems. In order to overcome these drawbacks, several solid acid[3-15]catalysts have been widely applied in the synthesis of BPF such as H-beta, MCM-41, SBA-15. Although solid acid catalysts showed great catalytic performance, the deactivation phenomena limits their usage in continuous catalytic reaction. Therefore, it is desirable to further develop for the synthesis of bisphenol F.

Polyvinyl chloride (PVC) has been attracted sustained attention due to its structural stability and modifiability, and is recognized as a promising functional material for catalysis application.^[16-22] Typically, chemically modified PVC materials show good catalytic performance in some important organic reactions. For example, the composite material formed by palladium supported on polyamine modified PVC is used as catalyst for Suzuki reaction^[16] and Heck reaction^[17], which catalytic activity remains after 7 times of reused, EDA modified PVC material has also great catalytic performance after introducing hydrogen sulfate. In addition, the functional PVC has not been used in the synthesis of BPF. Therefore, it is a great

potential for applying the functional PVC in the synthesis of BPF.

Herein, we prepared a novel catalyst (PVC-EDA-SO₄H) (Scheme 1) by nucleophilic substitution with PVC and EDA to form basic polymeric material (PVC-EDA), followed via neutralization reaction to anchor acid groups of hydrogen sulfate, The as-prepared catalyst was characterized by Physicochemical method, and catalytic performance of the catalyst was investigated by condensation of phenol with formaldehyde to bisphenol F.

2. Experimental

2.1. Preparation of catalyst

The preparation of catalyst is presented in scheme 1.

Synthesis of the EDA-modified PVC. PVC (5.00 g) was swelled in anhydrous ethanol (8 ml) at room temperature for 30 mins, EDA (14.57 g) was slowly added and stirred at 80 °C for 8 h, the mixture was filtered to obtain crude product, then washed with dilute solution of sodium hydroxide and deionized water to remove the generated HCl and unreacted EDA. The PVC-EDA was obtained under drying at 60 °C for 24 h in vacuum.

Synthesis of the PVC-EDA-SO₄H. PVC-EDA (1 mol) and sulfuric acid (4 mol) were treated by ultrasound at room temperature for 1h, the mixture was filtered to obtain the crude product, then washed with deionized water until filtrate is neutral of pH. After drying at 60 °C for 24 h in vacuum, The PVC-EDA-SO₄H was obtained.

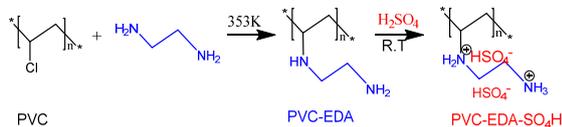
2.2. Catalyst characterization

Fourier transform infrared (FT-IR) spectra was measured using a Nicolet Avatar370 spectrophotometer in the scan

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range of 500-4000 cm⁻¹. Element analysis (EA) was carried out by ELEMENTAR VARIO EL III elements analyzer and TSN-2000 Sulfur and nitrogen analyzer. The acid amount of the catalyst was evaluated by a traditional acid-base titration.

Thermogravimetric and differential thermogravimetric (TGA-DTG) was measured using NETZSCH STA409 PC simultaneous thermal analyzer with a heating rate of 10 °C /min from 20 °C to 800 °C.



Scheme 1. The preparation of PVC-EDA-SO₄H

2.3.Catalytic testing

The synthesis of BPF over the catalyst was performed in a magnetically stirred round-bottomed flask with a reflux condenser and a digital temperature controller. In a typical experiment, the selected catalyst (0.5 wt% formaldehyde), phenol (18.80 g) and 37% aqueous formaldehyde (0.80 g) were stirred at 80 °C for 1h. After that, cooled to ambient temperature and filtrated to recover catalyst. The unreacted formaldehyde was evaluated from by acetylacetone spectrophotometric method using the Shimadzu UV-2450 spectrophotometer. Quantitative analysis of the BPF products was via the external standard method performed with the was determined by an Agilent 1100 HPLC equipped with under the test conditions of a UV detection and Venusil C18 column (4.6 mm×250 mm). The mobile phase of V(methanol/water) was 65:35, and flow rate 1.0 ml/min. The UV detection wavelength was 275 nm and column temperature was 30 °C. The catalyst activity was evaluated from the conversion of formaldehyde (FA) and the selectivity of BPF.

3. Results and discussion

3.1.Characterization of PVC-EDA-SO₄H

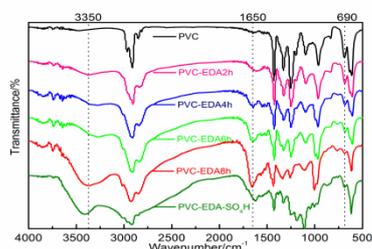


Fig.1 FT-IR spectra of PVC, PVC-EDA and PVC-EDA-SO₄H. The effect of different amonification time on the synthesis PVC-EDA was investigated by FT-IR and semi-quantitative analysis. As shown in Fig.1, With the increase of amonification time, the intensity of the characteristic vibration band of -NH₂- group (at around 1650 cm⁻¹) is significantly enhanced, while the intensity of the characteristic vibration band of C-Cl (at around 690 cm⁻¹) decreased, indicating that the increase of amonification

time is more conducive to the production of more alkaline sites. Therefore, PVC-EDA-SO₄H was prepared by acid-modifying PVC-EDA -8 h. as shown in the FT-IR curve of PVC-EDA-SO₄H, after acid-modifying PVC-EDA-8h, appearing new characteristic vibration bands at around 1080 cm⁻¹ and 1190 cm⁻¹, which are associated with the stretching vibration of S=O in HSO₄⁻. It suggests that sulfuric acid was successfully anchored on PVC-EDA.

Table.1 The element content and acid properties of samples

Samples	Element content (wt%)				Acid amount (mmol/g)
	C	Cl	N	S	
PVC	37.97	54.61	-	-	-
EDA-PVC	46.95	33.98	7.22	-	-
PVC-EDA-SO ₄ H	41.72	28.56	6.05	4.63	1.12

The contents of nitrogen in PVC, EDA-PVC and PVC-EDA-SO₄H were analyzed with elemental analyzer. As shown in Table 1, the Cl content of EDA-PVC was obviously decreased, and the N content of EDA-PVC was increased to 7.22% by the amonification of PVC. After treated with sulfuric acid, S content of PVC-EDA-SO₄H was increased to 4.63%, and the acid amount of it is 1.12 mmol/g, which indicated that HSO₄⁻ was anchoring on PVC-EDA successfully.

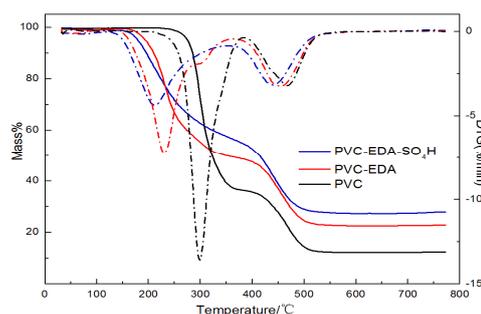


Fig. 2 TG- DTG analysis of PVC, PVC-EDA and PVC-EDA-SO₄H

The TG-DTG curves obtained for PVC, PVC-EDA and PVC-EDA-SO₄H are shown in Fig. 2, there are two distinct steps of weight losses for the three substances. The first weight loss occurs in the range of 200 - 300 °C is attributed to the removal of HCl from free radical mechanism. The second weight loss at around 450°C, which is attributed to the thermal decomposition of the skeleton. In addition, the all results show that the overall weight loss of PVC is reduced after modification, indicating that the thermal stability of PVC-EDA-SO₄H has improved to a certain extent.

3.2.Catalytic performance of PVC-EDA-SO₄H

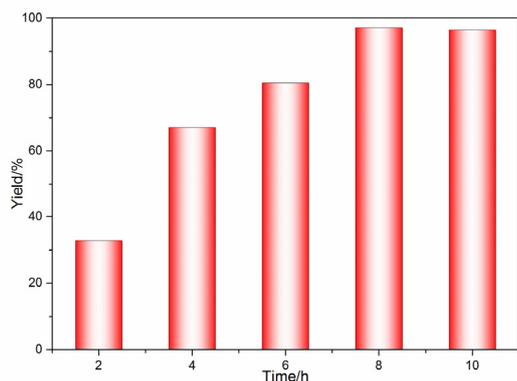


Fig.3 Effect of ammonification time on the performance of PVC-EDA-SO₄H catalyst

Reaction condition: n(Phenol / Formaldehyde) , 20:1; catalyst concentration, 1.0 wt.%; Reaction temperature, 80 °C; Reaction time, 4h.

The effect of catalyst's ammonification time on the synthesis of BPF was evaluated and results were shown in Fig. 3. The results suggest that ammonification time of catalyst plays an important role in the formation of BPF, when the ammonification time is extended from 2 h to 8 h, the yield of BPF gradually increases from 33.5 to 97.12 %, When the time prolongs to 10 h, the yield has no noticeable change. Indicating that appropriate extension time is beneficial to increase more alkaline sites in PVC, which promotes catalyst to form more catalytic active sites.

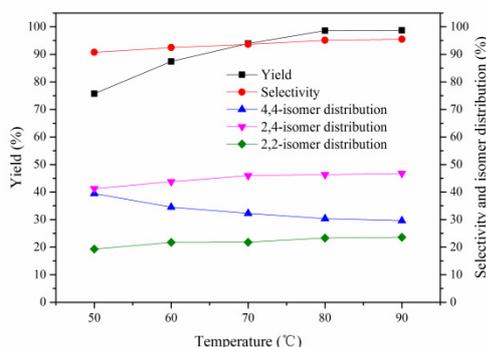


Fig. 4 Effect of reaction temperature on the synthesis of BPF. Reaction condition: n (Phenol / Formaldehyde) , 20:1; catalyst concentration, 1.0 wt.%; Reaction time, 1h.

The effect of reaction temperature on the synthesis of BPF is presented in Fig.4, With an increase of reaction temperature from 50 to 80 °C, the yield of BPF shows obviously increase from 75.7 % to 98.6 % with over 95.0 % selectivity for BPF, and the selectivity of 4,4' -isomer decreases from 39.5 % to 30.3 %, while the selectivity of 2,4' -isomer and 2,2' -isomer increases from 41.0 % to 46.4 % and 19.3 % to 23.3 %. Further increase in the temperature up to 90 °C, the yield has slight decrease, this might be because that the high temperature allows formaldehyde to escape from the system. Meanwhile, increasing of temperature only had a slight effect on the distribution of isomers, with kinetically controlled the 4,4' -isomer and thermodynamically controlled the other isomers remain the previous trend.

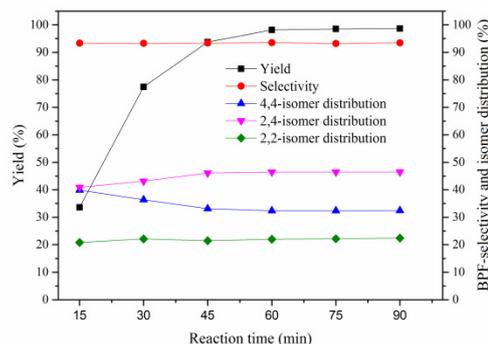


Fig. 5 Effect of reaction time on the synthesis of BPF.

Reaction condition: n (Phenol / Formaldehyde) , 20:1; catalyst concentration, 1.0 wt.%; Reaction temperature, 80 °C.

The effect of reaction time on the synthesis of BPF is shown in Fig.5. With an increase of reaction time from 15 to 45 min, the yield of BPF presents distinctly increase from 33.6 % to 93.7 % with over 93.0 % selectivity for BPF, and the selectivity of 4,4' -isomer decreases from 39.9 % to 33.11 %, while the selectivity of 2,4' -isomer and 2,2' -isomer increases from 40.8 % to 46.1 % and 19.3 % to 20.8 %. Further increase in the time up to 90 min, the reaction has been complete, meanwhile, increasing of temperature only had a slight effect on the distribution of isomers.

Table 2. Effect of catalyst amount on the synthesis of BPF

Catalyst concentration (wt%)	Yield (%)	Selectivity (%)	BPF isomer distribution (%)		
			4,4'	2,4'	2,2'
0	1.93	-	40.64	40.94	18.42
0.02	49.19	90.75	34.11	45.17	20.72
0.1	85.85	93.34	32.28	46.54	21.18
0.5	99.19	93.75	31.89	46.64	21.47
2.5	98.45	93.84	31.14	46.95	21.91

Reaction condition: n (Phenol / Formaldehyde) , 20:1; Reaction time, 1h, Reaction temperature, 80 °C.

The effect of catalyst concentration on the synthesis of BPF was presented in Table 2. when the catalyst concentration is 0.1 wt%, the yield of BPF can reach over 85.85 % with over 93.0 % selectivity, indicating that this new catalyst is highly-efficient for this reaction. Further increase in the catalyst concentration up to 0.5, the reaction has been almost complete, which the selectivity for mainly isomer of 2,4'-bisphenol F remains at round 46.6 %. With a further increase of the catalyst concentration, the yield of BPF slight decreases, this might be because that the increase of the amount of catalyst increases the mass transfer resistance.

The catalyst was recycled for 6 times via filtrating and adding into the reused catalyst to balance the mechanical loss, the reusability of catalyst on the synthesis of BPF is studied in Fig.6. Apparently, there are no significant changes between the yield and the isomer distribution of BPF, indicating that the catalyst can still remain effective catalytic activity after in the six runs.

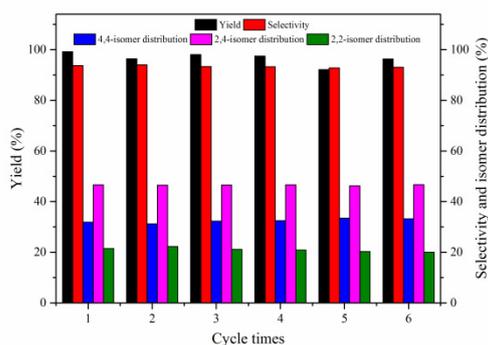


Fig. 6 Reusability of catalyst on the synthesis of BPF.

Reaction condition: n (Phenol / Formaldehyde), 20:1; catalyst concentration, 0.5 wt.%; Reaction temperature, 80 °C; Reaction time, 1h.

4. Conclusions

In this work, a novel PVC anchoring HSO_4^- was successfully synthesized by simple nucleophilic substitution and neutralization reaction. The as-prepared catalyst was characterized, which results that hydrogen sulfate ions were successfully anchored in the PVC-EDA. Therefore, the catalyst exhibited high activity and stability in the synthesis of bisphenol F, and achieved almost total conversion of formaldehyde and selectivity (94%) of bisphenol F under the optimal reaction conditions of phenol/formaldehyde 20, catalyst concentration 0.5, reaction temperature 80 °C and reaction time 1h. Moreover, the catalyst was reused six runs without a significant loss. In summary, It is hoped that this catalyst can be used as a promising material to achieve a new environmentally benign catalytic system.

Acknowledgements

This study was supported by the National Natural Science Foundation of China (Grant Nos. 21975070, 21776068).

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