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Alkylation of Hydroquinone with *tert*-Butanol Catalyzed by Polymer-supported Sulfonimide

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Abstract Polystyrene with pendant perfluorobutylsulfonylimide (PPFSI) was developed as a novel polymer-supported strong acid catalyst for alkylation of hydroquinone (HQ) with *tert*-butanol (TBA), and highly selective synthesis of 2-*tert*-butyl hydroquinone (2-TBHQ) was investigated over PPFSI under various experiment conditions. When the molar ratio of TBA to HQ was 1.2:1, using 3 mol% of PPFSI as catalyst in 1,2-dichloroethane at 130 °C for 5 h, the maximum of selectivity (85.9%) of 2-TBHQ was obtained while the conversion of HQ was 76.7%. Compared with other solid acid catalysts PPFSI was found to be a very effective and reusable catalyst for alkylation of hydroquinone with *tert*-butanol.

Keywords Polymer-supported · Brønsted acid · Perfluorobutylsulfonylimide · 2-*tert*-Butylhydroqinoe · 2,5-Di-*tert*-butylhydroqinoe · Alkylation

1 Introduction

2-*tert*-Butylhydroquinone (2-TBHQ) is an excellent phenolic antioxidant for non-food fats, oils, and unstable organic solvents due to its extraordinary anti-oxidation property and low toxicity [1–3]. It is also a very important intermediate used in pharmaceuticals and photographic plates, as well as is used as heat stabilizers for plastics and rubbers [4]. To prepare this compound, liquid mineral acids such as sulfuric acid, aromatic sulfonic acid and phosphorous acid are conventionally utilized as catalysts for alkylation of hydroquinone (HQ) [5–8]. Though good yields and high products selectivity were reached, but they led to excessive acid waste streams and heavy corrosion of equipments. Therefore, many efforts have been done for developing new catalytic process and employing environmentally benign solid acid catalysts to replace the environmentally hazardous materials since 1980s [9–14]. More recently, Xu et al. reported the alkylation of hydroquinone with *tert*-butanol using silica molecular sieves catalysts (AlSBA-15, MSU-$S_{(BEA)}$) [15, 16] and Gagea et al. studied this reaction using silica-immobilized triflate derivatives as the catalysts [17]. Both groups obtained good results in terms of selectivity for 2-TBHQ but only at moderate conversions.

Although the polymer-supported Brønsted acids are one of important solid acid catalysts, there are few literatures dealing with the polymer-supported Brønsted acid catalysts for the alkylation of hydroquinone with *tert*-butanol till now. On the other hand, as the high acid strength [18], the polymers containing sulfonimide groups have recently received considerable attention in the development of new polymer-supported Brønsted acids [19–21].

In this paper, polymer-supported strong Brønsted acid, polystyrene with pendant perfluorobutylsulfonylimide group (PPFSI), was used as heterogeneous catalyst and its catalytic performances to the alkylation of hydroquinone with *tert*-butanol (TBA, Eq. 1) were investigated.

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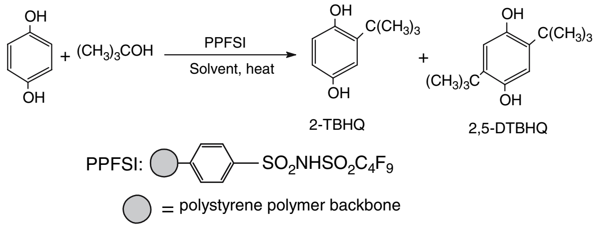


(1)

2 Experimental

2.1 Catalyst Preparation

The catalyst, PPFSI, was prepared following the procedures in a previous work [21]. Triethylamine (5 mL, 0.033 mol) was careful dropwise into the mixture of polystyrylsulfonyl chloride resin (5 g, loading of $–SO_2Cl = 2.85$ mmol/g) and $C_4F_9SO_2NH_2$ (28.5 mmol) in 50 mL of 1,2-dichloroethane, heated at 60 °C for 48 h with stirring under an atmosphere of argon, filtered, washed successively with $CHCl_3$, HCl, H_2O, and dried in vacuo at 80 °C for 24 h. 7.32 g of polymer was obtained (ca. 70% yield).

2.2 Characterization of Catalyst

The structure of PPFSI was characterized by FT-IR spectrum. IR (KBr,ν, cm^{-1}): 3416, 1632 (N–H); 3064, 1601, 1451, 1413 ($–C_6H_5$); 1372, 1175 ($–SO_2–$); 1237 (C–F).

Acid content of PPFSI was determined by acid-base titration. To a suspension of the PPFSI in H_2O-EtOH (1:1) was added a standard NaOH solution. After the mixture was stirred for 2 h, a 0.01% solution of phenolphthalein in EtOH was added to the suspension as an indicator. The solution was titrated with a standard HCl solution. The acid loading of the PPFSI was determined by several parallel experiments.

Its acid strength was measured by the Hammett indicator method [22]. The PPFSI was pretreated by being evacuated at 393 K for 2 h, then cooled to room temperature and allowed to contact the vapor of the Hammett indicator. The acid strength was determined by observing the color change of the indicator adsorbed on the surface of the PPFSI. The anthraquinone ($H_0 = -8.2$), *p*-nitrotoluene ($H_0 = -11.35$) and 4-chloronitrobenzene ($H_0 = -12.70$) were used as indicators and benzene was used as the solvent.

2.3 Catalytic Reactions

A typical experiment procedure for alkylation of hydroquinone is as follows: 0.330 g of hydroquinone (3.0 mmol), 0.09 mmol of PPFSI (based on loading of H^+ and dried at 60 °C under reduced pressure for 6 h in advance), freshly distilled 1,2-dichloroehnane (3.0 mL, as solvent), *tert*-butanol (3.6 mmol), and *n*-decane (1.54 mmol, as internal standard) were in turn introduced into a pressure-tolerant sealed tube equipped with magnetic stirrer, the mixture was then agitated at designated temperature for prescriptive time. After being filtrated off, washed with acetone and dried at 100 °C for 2 h, the solid catalyst could be directly used for next run while the filtrate was diluted with acetone and then analyzed by GC 9790 gas chromatograph (FULI Company) equipped with a 30QC3/AC225 capillary column (SGE Company) and a flame ionization detector using programmed temperature from 60 to 220 °C.

In order to determine the isolated yields of alkylation products, the solvent was removed from organic phase under reduced pressure and the remainder was purified by a silica gel (200–300 mesh) column chromatograph (eluent: petroleum ether/EtOAc = 4/1). Products were characterized by ^1H NMR, ^{13}C NMR and FT-IR spectra.

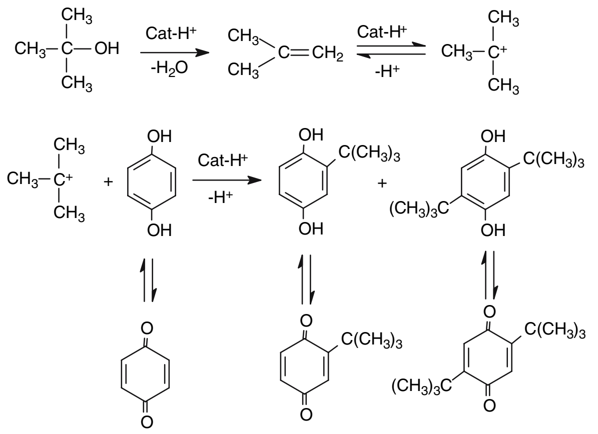
3 Results and Discussion

3.1 Acid Content and Acidic Strength of PPFSI

The acid loading of PPFSI was found to be 3.02 mmol/g by several parallel measurements. The acid strength was determined by observing the color change of the indicator adsorbed on the surface of the PPFSI. The H_0 value of PPFSI was obtained in range of from −8.2 to −11.35, which showed that the PPFSI was a strong Brønsted acid catalyst.

3.2 Mechanism of *tert*-Butylation of Hydroquinone

The general reaction scheme is given in Scheme 1. The *tert*-butylation of hydroquinone with *tert*-butanol is an electrophilic substitution reaction on the aromatic ring commonly via a carbenium ion mechanism [23]. In the presence of acid catalyst at high temperatures, *tert*-butanol gets dehydrated into isobutylene and water. Isobutylene is subsequently protonated by the acid catalyst to form *tert*-butyl carbenium, which further reacts with hydroquinone to generate 2-*tert*-butyl hydroquinone (2-TBHQ) and 2,5-di-*tert*-butyl



Scheme 1 Reaction mechanism of *tert*-butylation of hydroquinone

hydroquinone (2,5-DTBHQ). Because both material (HQ) and alkylated products (2-TBHQ and 2,5-DTBHQ) are easily oxidated, so we detected the existence of oxidated products of these substances during the experiments.

No *O*-alkylation products were found in our study. Badamali et al. [24] considered that only weak acid sites can favor formation of *O*-alkylation product, and Yadav et al. [14, 25] thought that the ratio of different products depends on the nature of catalysts and reaction conditions used for alkylation. According to these viewpoints, there should be no *O*-alkylation hydroquinone producing in the presence of strong acidic PPFSI.

3.3 Effect of Reaction Time

The effects of reaction time on *tert*-butylation of hydroquinone in the presence of 3 mol% PPFSI were investigated with a range from 1 to 6 h (Fig. 1).

As shown in Fig. 1, the conversion of hydroquinone increased with increasing reaction time, but the selectivity of 2-TBHQ attained the maximum at 3.5 h. Overly-prolonged time (>4 h) could cause a drastic decrease of 2,5-DTBHQ, which was favorable for formation of desirable 2-TBHQ. Therefore, the highest yield of 2-TBHQ (65.9%) was obtained at about 5 h.

3.4 Effect of Reaction Temperature

Of various reaction conditions, temperature is one of the most important factors that will affect not only the conversion of HQ but also the distribution of products. The influence of the reaction temperature was studied over the PPFSI catalyst. From the results in Table 1, it showed that increasing temperature the conversion of HQ was decrease under the experiment conditions, but the selectivity of 2-TBHQ was exactly the reverse. When the reaction temperature was increased from 110 to 140 °C, the selectivity of 2-TBHQ could be up from 71% to 93.4% and at the same time, the selectivity of 2,5-DTBHQ decreased from 29% to 6.6%. The high reaction temperature was favorable for the formation of 2-TBHQ due to the strong acidity of PPFSI. At higher reaction temperature, de-*tert*-butylation will be promoted and more 2,5-DTBHQ is converted to 2-TBHQ and less 2-TBHQ is converted to 2,5-DTBHQ in the existence of the strong acid catalyst [26]. It resulted in the selectivity of 2-TBHQ up to 93.4% at 140 °C. To take the thermal stability of PPFSI and some other factors into account, 130 °C was selected as the reaction temperature.

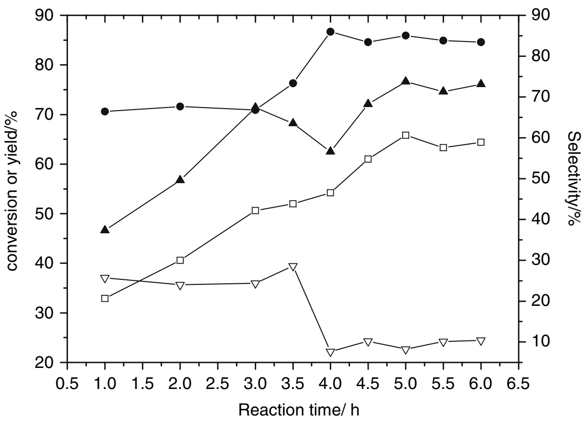


Fig. 1 Effects of reaction time on *tert*-butylation of hydroquinone: ●, selectivity of 2-TBHQ; ▲, conversion of HQ; □, yield of 2-TBHQ; ▽, selectivity of 2,5-DTBHQ. Reaction conditions: 3.0 mmol of HQ, 1.2 equiv. of TBA, 3 mol% PPFSI, $(CH_2Cl)_2$ as solvent (3 mL), 130 °C

3.5 Effect of Solvents

As indicated in Table 2, 1,2-dichloroehnane and toluene were better solvents than others such as nitroethane, 1,4-dioxane and butanone in view of the conversion of HQ. Although the conversion of HQ in toluene was as high as 85%, its selectivity of 2-TBHQ was not satisfying. 1,2-Dichloroehnane was found to be the suitable solvent in our study for alkylation of hydroquinone with *tert*-butanol. The polarity (generally measured by dielectric constant ε) and the coordinating property (associated with accept number AN and donor number DN) might be the main factors for the influence of solvents [27]. In the cases of 1,4-dioxane and butanone as solvents the conversions of HQ were poor and the mainly products were found to be the oxidated compounds.

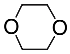
Table 1 Effect of reaction temperature[a]

Entry	Temperature (°C)	Conversion of HQ (%)	Selectivity (%)			Yield (%) 2-TBHQ
			2-TBHQ	2,5-DTBHQ	Others[b]	
1	110	84.6	71	21.7	7.3	60.0
2	120	80.1	78.2	16.4	5.4	62.6
3	130	76.7	85.9	8.2	5.9	65.9
4	140	68.8	93.4	1.4	5.2	64.2

[a] Reaction conditions: TBA:HQ = 1.2:1, PPFSI 3 mol% as catalyst, 5 h, 3 mL $(CH_2Cl)_2$ as solvent; The conversion of HQ and the yield of 2-TBHQ were determined by GC using *n*-decane as internal standard

[b] Including various oxidated products and longer alkyl substituted hydroquinones

Table 2 Effect of solvents[a]

Entry	Solvent	Conversion of HQ (%)[b]	Selectivity (%)			Yield of 2-TBHQ (%)[b]
			2-TBHQ	2,5-DTBHQ	Others	
1	CH_2ClCH_2Cl	76.7	85.9	7.2	5.9	65.9
2	$C_6H_5CH_3$	84.5	50.9	4.7	44.4	43.0
3	$CH_3CH_2NO_2$	24.5	51.6	32.0	16.4	12.6
4	$CH_3COCH_2CH_3$	33.3	18.7	0.0	81.3	6.2
5		35.3	23.1	2.1	74.8	8.1

[a] Reaction conditions: TBA:HQ = 1.2:1, PPFSI 3 mol% as catalyst, 5 h, 3 mL $(CH_2Cl)_2$ as solvent

[b] The conversion of HQ and the yield of 2-TBHQ were determined by GC using *n*-decane as internal standard

3.6 Effect of Dosage of Catalyst

The influence of amount of catalyst is list in Table 3. The results showed that PPFSI was a very effective catalyst for alkylation of hydroquinone with *tert*-butanol and even if 1 mol% of PPFSI was used the conversion of HQ and yield of 2-TBHQ could be up to 84.5% and 58.7%, respectively. We can see that the higher dosage of catalyst (10 mol%) was not favorable for both selectivity and yield of 2-TBHQ. The optimal dosage was 3 mol% with which the target product 2-TBHQ could attain a yield as high as ca. 65.9%.

3.7 Effect of Molar Ratio of *tert*-Butanol to Hydroquinone

In order to investigate the effect of material ratio, the TBA to HQ molar ratio was varied between 0.7:1.0 and 2.5:1.0 under otherwise reaction conditions were maintained in the presence 3 mol% PPFSI. As shown in Table 4, the conversion of HQ could be up to 99.6% with increasing molar ratio of TBA to HQ to 2.5:1, but the selectivity of 2-TBHQ decreased rapidly due to the increasing dialkylated product, since excess TBA continued to react with 2-TBHQ to give 2,5-DTBHQ (selectivity 71.5%). By the way, it was found

Table 3 Effect of dosage of catalyst[a]

Entry	Amount of Catalyst (mol%)[b]	TBA:HQ	Conversion of HQ (%)	Selectivity (%)			Yield of 2-TBHQ (%)[c]
				2-TBHQ	2,5-DTBHQ	Others	
1	1	1.2:1	84.5	69.5	21.6	8.9	58.7
2	3	1.2:1	76.7	85.9	8.2	5.9	65.9 (61.1)[d]
3	5	1.2:1	80.1	78.2	14.6	5.2	62.6
4	10	1.2:1	77	74.1	20.3	5.6	57.0

[a] Reaction conditions: 3.0 mmol of HQ, $(CH_2Cl)_2$ as solvent (3 mL), 130 °C, 5 h

[b] Dosage is based on the amount of H^+

[c] Determined by GC using *n*-decane as internal standard

[d] Isolated yield in parenthesis

Table 4 The results of molar ratio of hydroquinone to *tert*-butanol[a]

Entry	Amount of Catalyst (mol%)[b]	TBA:HQ	Conversion of HQ (%)	Selectivity (%)			Yield of 2-TBHQ (%)[c]
				2-TBHQ	2,5-DTBHQ	Others	
1	3	0.7:1	51.8	84.4	6.5	9.1	43.7
2	3	1.2:1	76.7	85.9	8.2	5.9	65.9 (61.1)[d]
3	3	1.5:1	82.8	78	15.3	6.7	64.5
4	3	2.0:1	94	43	50.7	6.3	40.4
5	3	2.5:1	99.6	13.7	71.5	14.8	13.6
6	3	1.2:1[e]	78.2	80.3	12.7	7.0	62.7

[a] Reaction conditions: 3.0 mmol of HQ, $(CH_2Cl)_2$ as solvent (3 mL), 130 °C, 5 h

[b] Dosage is based on the amount of H^+

[c] Determined by GC using *n*-decane as internal standard

[d] Isolated yield in parenthesis

[e] Methyl *tert*-butyl ether was the alkylating reagent

that methyl *tert*-butyl ether (MTBE) was as good the alkylating reagent as TBA for forming 2-TBHQ under similar reaction conditions (Entry 6). The optimal molar ratio of *tert*-butanol to hydroquinone was found to be 1.2:1.0 for 2-TBHQ.

3.8 Comparison of Different Solid Acid Catalysts

The comparison results of different homogeneous or solid acid catalysts with PPFSI are showed in Table 4. For both Nafion NR50 and ion-exchange resin, NKC-9, only

Table 5 Comparison of different solid acid catalysts[a]

Entry	Catalyst, mol%[b]	TBA:HQ	Conversion of HQ (%)	Selectivity (%)			Yield of 2-TBHQ (%)[c]
				2-TBHQ	2,5-DTBHQ	Others	
1	PPFSI, 3	1.2:1	76.7	85.9	8.2	5.9	65.9
2	NKC-9, 20	1.2:1	72	62	27.8	10.2	44.6
3	Amberlyst-15, 10	1.2:1	36.4	88.4	6.6	5.0	32.1
4	Nafion NR50, 20	1.2:1	61.3	77.1	18.6	4.3	47.2
5	85% H_3PO_4, 50	1.3:1	45.3	78.2	16.9	4.9	35.4

[a] Reaction conditions: catalyst × equiv. relative to hydroquinone, 5 h, 3 mL $(CH_2Cl)_2$ as solvent and 130 °C for PPFSI, 120 °C for other catalysts

[b] Dosage is based on the amount of H^+

[c] Determined by GC using *n*-decane as internal standard

Table 6 Reusability of catalyst at 130 °C[a]

Run	Conversion of HQ (%)	Selectivity (%)			Yield of 2-TBHQ (%)
		2-TBHQ	2,5-DTBHQ	Others	
1	76.7	85.9	8.2	5.9	65.9
2	76.9	81.7	13.1	5.2	62.8
3	78.9	78.6	16.4	5.0	62.0
4	73.4	82.6	14.6	2.8	60.6
5	73.2	83.8	10.0	6.2	61.3
6	72.4	80.5	12.5	7.0	58.2

[a] Reaction conditions: TBA:HQ = 1.2:1, PPFSI 3 mol% as catalyst, 5 h, 3 mL $(CH_2Cl)_2$ as solvent; The conversion of HQ and the yield of 2-TBHQ were determined by GC using *n*-decane as internal standard

moderate conversion of HQ (61.3% and 72%) and selectivity of 2-TBHQ (77.1% and 62%) could be obtained although 20 mol% of catalysts was used. In the case of Amberlyst-15, the conversion of HQ was poor but the selectivity of 2-TBHQ was high (88.4%). Of all the catalysts PPFSI was found to be the most effective catalyst for alkylation of hydroquinone with *tert*-butanol and it was much more effective than 85% H_3PO_4 as catalyst under similar conditions.

3.9 Reusability of Catalyst

When alkylation of hydroquinone with *tert*-butanol finished, PPFSI could be recovered via simple filtration without tedious disposal. The catalytic performances of recovered catalysts are listed in Table 5. PPFSI showed a very good reusability and its high activity and steady selectivity could be maintained at least 6 runs at 130 °C (Table 6).

4 Conclusions

PPFSI was developed as a novel polymer-supported strong acid catalyst for alkylation of hydroquinone with *tert*-butanol, and highly selective synthesis of 2-*tert*-butyl hydroquinone was investigated over PPFSI under various experiment conditions. When the molar ratio of TBA to HQ was 1.2:1, using 3 mol% of PPFSI as catalyst in 1,2-dichloroethane at 130 °C for 5 h, the maximum of selectivity (85.9%) of 2-TBHQ was obtained while the conversion of HQ was 76.7%. Compared with other solid acid catalysts PPFSI was found to be a very effective and reusable catalyst for alkylation of hydroquinone with *tert*-butanol.

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