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ORIGINAL PAPER

Synthesis of the strongly acidic sulfonated condensed polynuclear aromatic (S-COPNA) resins using aromatic aldehydes as cross-linking agents

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Abstract In the presence of 5 wt% of *p*-toluenesulfonic acid (TsOH), the mixture (TPA/PR = 1.5/1.0) of pyrene (PR) and terephthalaldehyde (TPA) was heated at 160 °C for 1.5 h under nitrogen to give the condensed polynuclear aromatic (COPNA) resin. It was transformed to an infusible and insoluble solid by further heating at 300 °C for 1 h. The obtained material was treated with sulfuric acid at 80 °C for 15 h under nitrogen to give the sulfonated COPNA(PR,TPA) resin. The sulfonated COPNA(PR,BA/TPA) resin was prepared by heating the mixture of PR, benzaldehyde (BA), and a small amount of TPA in the presence of TsOH followed by the treatment with sulfuric acid. The sulfonated COPNA(PR,TPA) resin was reused without significant loss of activities, and exhibited the higher performance than conventional solid acids.

Keywords COPNA resin · Acid catalysts · Protonic acids · Aromatic aldehydes · Sulfonated polymers

Introduction

In 1986, Otani et al. [1–5] have reported the synthesis of the condensed polynuclear aromatic (COPNA) resins with extremely high thermostability through the dehydration reaction between fused aromatic hydrocarbons and *p*-xylylene glycol (1,4-benzenedimethanol) (PXG) catalyzed by *p*-toluenesulfonic acid (TsOH). After that, they have reported the preparation of the new COPNA resins with a different

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type of linkage from other than the xylylene bond, using aromatic aldehydes such as terephthalaldehyde (TPA) [6, 7] and benzaldehyde (BA) [8] as cross-linking agents.

We have reported [9] the synthesis and evaluation of the sulfonated COPNA (S-COPNA) resins as strong polymeric protonic acids [10–25] using PXG as the cross-linking agent. Activities of the S-COPNA resins were much higher than those of conventional solid acids. The S-COPNA resins were insoluble to boiling water and many hot organic solvents, and reused without significant loss of activities. As an extension of our work [9], we were interested in the properties of the new S-COPNA resins which possessed the different type of linkage and terminal groups using TPA and BA as the cross-linking agents. In this article, the results for the synthesis and evaluation of these S-COPNA resins are described.

Experimental section

Materials

TsOH, BA, dichloromethane, ethanol, acetic acid, benzoic acid, sulfuric acid, fuming sulfuric acid, and chlorosulfonic acid were purchased from Wako Pure Chemical Industry (Osaka, Japan). PR, TPA, cyclohexyl acetate, oleyl acetate, and *p*-methylbenzaldehyde were purchased from Tokyo Chemical Industry (Tokyo, Japan). NP was purchased from Aldrich (WI, USA). They were used as received. Test paper (Merckoquant, sulfate test) was purchased from Merck (Germany). Column chromatography was performed on Wakogel C-200.

Preparation of the post-cured COPNA(PR,TPA) resin

The mixture of PR (16.2 g, 80 mmol), TPA (16.1 g, 120 mmol), and TsOH (1.61 g, 5 wt% of [PR + TPA]) was heated at 160 °C for 1.5 h in a stream of nitrogen to produce a highly viscous material. The yield was 30.4 g (96%).

The obtained material was converted into an infusible and insoluble solid by further heating at 300 °C for 1 h under nitrogen. The obtained solid was ground to a powder by the mill. The yield was 29.3 g (92%); IR (KBr) ν_{max} 3033 (ArH), 2821, 2725, 1698 (CHO), 1602, 834 cm^{-1} (ArH). The nominal sample composition was determined by elemental analysis to be $CH_{0.570}O_{0.079}$.

Preparation of the post-cured COPNA(PR,BA/TPA) resin

The mixture of PR (20.2 g, 100 mmol), BA (8.5 g, 80 mmol), TPA (2.68 g, 20 mmol), and TsOH (1.57 g, 5 wt% of [PR + BA + TPA]) was heated at 160 °C for 2 h in a stream of nitrogen to produce a highly viscous material.

It was converted into an infusible and insoluble solid by further heating at 300 °C for 1 h. The obtained solid was ground to a powder. The yield was 29.0 g (93%); IR (KBr) ν_{max} 3035 (ArH), 1698 (CHO), 1600, 1491, 840 cm^{-1} (ArH). The nominal sample composition was determined by elemental analysis to be $CH_{0.548}O_{0.027}$.

Sulfonation of the post-cured COPNA(PR,TPA) resin by sulfuric acid

The post-cured COPNA(PR,TPA) resin (2.5 g) was added to sulfuric acid (20 mL). The mixture was stirred at 80 °C for 15 h under nitrogen. The mixture was poured into distilled water (133 mL). The precipitate was collected by filtration and washed repeatedly with hot distilled water (>80 °C) until the wash water reached a pH of 7. The precipitate was dried at 150 °C for 3 h under reduced pressure. The S-COPNA(PR,TPA) resin (2.8 g) was obtained as the hygroscopic black powder; IR (KBr) ν_{max} 1686 (CHO), 1637, 1604 (ArH), 1168, 1033 (SO_3H), 831 cm^{-1} (ArH). The nominal sample composition was determined by elemental analysis to be $CH_{0.576}O_{0.268}S_{0.027}$.

Acid density was determined by titration using the following procedure. The sulfonated polymer (168 mg) was placed in 0.1 M aqueous NaOH solution (20 mL), and the mixture was kept at room temperature for 1 day. The precipitate was filtered, and the filtrate was then back titrated with 0.1 M aqueous potassium hydrogen phthalate solution using phenolphthalein as an indicator.

Sulfonation of the post-cured COPNA(PR,BA/TPA) resin by sulfuric acid

The S-COPNA(PR,BA/TPA) resin (1.9 g) was prepared from the post-cured COPNA(PR,BA/TPA) resin (2.5 g) in a manner similar to the sulfonation of the post-cured COPNA(PR,TPA) resin by sulfuric acid; IR (KBr) ν_{max} 3034 (ArH) 1691 (CHO), 1599, 1490 (ArH), 1168, 1033 (SO_3H), 837 cm^{-1} (ArH). The nominal sample composition was determined by elemental analysis to be $CH_{0.575}O_{0.119}S_{0.010}$.

Preparation of the S-COPNA(PR,TPA) resin by fuming sulfuric acid

The S-COPNA(PR,TPA) resin (2.7 g) was prepared from the post-cured COPNA(PR,TPA) resin (2.5 g) in a manner similar to the sulfonation of the post-cured COPNA(PR,TPA) resin (2.5 g) by sulfuric acid; IR (KBr) ν_{max} 1686 (CHO), 1603 (ArH), 1166, 1033 cm^{-1} (SO_3H).

Preparation of the post-cured COPNA(PR,PXG) resin [9]

The mixture of PR (20.2 g, 100 mmol), PXG (13.8 g, 100 mmol), and TsOH (1.70 g, 5 wt% of [PR + PXG]) was heated at 140 °C for 45 min in a stream of nitrogen to produce a highly viscous material. The yield was 31.6 g (98%).

It was converted into an infusible and insoluble solid by further heating at 300 °C for 1 h under nitrogen. The obtained solid was ground to a powder by the mill. The yield was 30.7 g (96%).

Preparation of the post-cured COPNA(NP,PXG) resin [9]

The mixture of NP (15.4 g, 120 mmol), PXG (16.6 g, 120 mmol), and TsOH (1.60 g, 5 wt% of [NP + PXG]) was heated at 120 °C for 3.5 h in a stream of nitrogen to produce a highly viscous material.

It was converted into an infusible and insoluble solid by further heating at 300 °C for 1 h. The obtained solid was ground to a powder. The yield was 25.5 g (87%).

Sulfonation of the post-cured COPNA(PR,PXG) resin by chlorosulfonic acid

A solution of chlorosulfonic acid (3.9 mL, 60 mmol) in dichloromethane (7.5 mL) was slowly added to the mixture of the post-cured COPNA(PR,PXG) resin (2.5 g) in dichloromethane (15 mL) with stirring under nitrogen. The mixture was stirred at 25 °C for 24 h. The precipitate was collected by filtration and washed with dichloromethane. The precipitate was dispersed in 0.5 M NaOH solution (200 mL) and stirred at 80 °C for 4 h. The mixture was filtered and the precipitate was washed with distilled water. The precipitate was dispersed in 2 M sulfuric acid solution (200 mL) and stirred at room temperature for 1 h. The mixture was filtered and the precipitate was washed with distilled water. The precipitate was heated at 150 °C for 3 h under reduced pressure. The precipitate was dispersed in distilled water (100 mL) and stirred at room temperature for 1 h. The mixture was filtered and the precipitate was washed with distilled water until the wash water reached a pH of 7. The precipitate was dried at 150 °C for 3 h under reduced pressure to give the sulfonated polymer. The yield was 3.0 g; IR (KBr) $\nu_{\max}$ 2925 (CH_2), 1637 (ArH), 1166, 1020 cm^{-1} (SO_3H). The nominal sample composition was determined by elemental analysis to be $CH_{0.671}O_{0.312}S_{0.086}$.

Sulfonation of the post-cured COPNA(NP,PXG) resin by chlorosulfonic acid

The S-COPNA(NP,PXG) resin (3.3 g) was prepared from the post-cured COPNA(NP,PXG) resin (2.5 g) in a manner similar to the sulfonation of the post-cured COPNA(PR,PXG) resin by chlorosulfonic acid; IR (KBr) $\nu_{\max}$ 2923 (CH_2), 1637 (ArH), 1126, 1021 cm^{-1} (SO_3H). The nominal sample composition was determined by elemental analysis to be $CH_{0.649}O_{0.365}S_{0.086}$.

Determination of the rate constant (*k*) for the esterification of carboxylic acids and the hydrolysis of esters

Esterification of acetic acid with ethanol was typically carried out at 80 °C in the mixture of ethanol (56.80 mL, 1.0 mol), acetic acid (5.71 mL, 0.1 mol), and the catalyst (200 mg). The reaction mixture at 10, 20, 30, 40, 50, 60, 80, 100, 120, and 140 min was analyzed by titration with 0.1 M aqueous NaOH solution. In the actual experiment, a blank sample containing EtOH (62.51 mL) and the catalyst (200 mg) without acetic acid was also titrated. From the difference in titrant volume required to reach the endpoint for the blank, the concentration of acetic acid was calculated. Rate constants were determined by the plots between time versus $[1/(a\text{-}b)]\ln[b(a-x)/a(b\text{-}x)]$ (the second order reaction) using the method of least squares. The rate constant of sulfuric acid was determined in the early stage of the reaction (10 min). The S-COPNA resins were dried at 150 °C for 1 h under reduced pressure prior to the reaction.

Esterification of benzoic acid with ethanol was carried out in the mixture of ethanol (56.80 mL, 1.0 mol) and benzoic acid (12.2 g, 0.1 mol) at 80 °C. The reaction mixture at 10, 20, 40, 60, 100, 140, 180, 220, 260, 300, 340, and 380 min was analyzed by titration with 0.1 M aqueous NaOH solution.

The hydrolysis of cyclohexyl acetate was carried out in the mixture of cyclohexyl acetate (0.64 mL, 4.4 mmol) and distilled water (59.40 mL, 3.3 mol) at 90 °C. The reaction mixture at 10, 20, 30, 40, 50, 60, 80, 100, 120, and 140 min was analyzed by titration with 0.005 M aqueous NaOH solution.

The hydrolysis of oleyl acetate was carried out in the mixture of oleyl acetate (1.57 mL 4.4 mmol) and distilled water (59.40 mL, 3.3 mol) at 100 °C. The reaction mixture at 10, 20, 30, 40, 50, 60, 80, 100, 120, 140, 160, and 180 min was analyzed by titration with 0.005 M aqueous NaOH solution.

Recycle experiments of the formation of ethyl acetate catalyzed by the S-COPNA resins

After esterification of acetic acid with ethanol for 4 h, the conversion of acetic acid was determined by acid titration of remaining AcOH with 0.1 M aqueous NaOH solution. The catalyst was recovered by decantation and reused repeatedly for the next reaction.

Sulfonation of *p*-methylbenzaldehyde in sulfuric acid

The mixture of *p*-methylbenzaldehyde (1.0 g) and sulfuric acid (8 mL) was stirred at 80 °C for 15 h under nitrogen. The solution was poured into ice water (53 mL). The mixture was extracted with ether. The extracts were washed with water, dried and evaporated and the residue was chromatographed (hexane–acetone = 10:1) on silica gel. *p*-Methylbenzaldehyde was recovered in 80%.

Characterization

IR spectra were recorded on a JEOL FT/IR-620 spectrophotometer. ^{1}H NMR spectra were measured on a Hitachi R-1200 spectrometer using tetramethylsilane as an internal standard. Thermogravimetric analysis (TGA) in air atmosphere was carried out on a Rigaku Thermo Plus 2 station TG-DTA TG 8120 at a heating rate of 10 °C/min. All samples were evacuated at 150 °C for 1 h under reduced pressure prior to the measurement of TGA. The grinding was conducted by Wonder Blender WB-1 (Osaka Chemical Co., purchased from AS ONE Co.).

Results and discussions

Synthesis of the S-COPNA(PR,TPA) resin

First, synthesis of the S-COPNA(PR,TPA) resin (TPA/PR = 1.0/1.0 in the molar ratio) (PR = pyrene) was investigated. The mixture of PR, TPA, and TsOH (5 wt%

of [PR + TPA]) was heated [26–33] at 160 °C for 1 h under nitrogen to give a highly viscous dark green melt (called as a B-stage resin) [6, 7]. The material was converted into an infusible and insoluble black solid by subsequent heating at 300 °C for 1 h under nitrogen [6, 7].

The post-cured COPNA resin was sulfonated by fuming sulfuric acid (15 wt% SO_3) at 80 °C for 15 h under nitrogen to give the corresponding S-COPNA resin as the black powder. Table 1 summarizes the results for the sulfonation of the post-cured COPNA resins with various molar ratios TPA/PR. Acid density was determined by acid titration. The rate constant (k) for the esterification of acetic acid with EtOH was determined by acid titration of remaining acetic acid included in the reaction mixture. The IR spectra for all S-COPNA resins showed the characteristic absorption at 1686 cm^{-1} attributed to the unreactive CHO groups. When the molar ratios TPA/PR became larger, the absorbance of the absorption at 1686 cm^{-1} increased, indicating that larger amounts of CHO groups were contained in the resin. Increase of the molar ratios TPA/PR resulted in the decrease of both the acid density and k (entries 1–5). It is probably because the benzene ring with the CHO group was not sulfonated. Conversely, the S-COPNA resins with TPA/PR = 1.0/2.0 and 1.0/1.5 were less active than that with TPA/PR = 1.0/1.0 in spite of larger acid densities although the reason is not clear (entries 1 and 2). The S-COPNA resin with TPA/PR = 1.0/1.0 possessed the highest activity, but it was partially soluble to boiling water (entry 3). The insoluble S-COPNA resin was obtained from the sulfonation of the post-cured COPNA resin with TPA/PR = 1.5/1.0 (entry 5). When the COPNA resin without post-curing was sulfonated, the S-COPNA resin was partially soluble to boiling water (entry 6). Sulfonation of the post-cured COPNA resin at 25 °C afforded the more active catalyst than 80 °C although the acid density was slightly lower (entries 5 and 7).

Table 1 Sulfonation of the post-cured COPNA(PR,TPA) resin by fuming sulfuric acid

Entry	TPA/PR	Temp (°C)	Acid density (mmol g^{-1})[a]	$k^{b} \times 10^{-4}$	Solubility[c]
1	1.0/2.0	80	5.11	6.43	+
2	1.0/1.5	80	5.11	7.60	+
3	1.0/1.0	80	4.92	8.04	++
4	1.25/1.0	80	4.39	7.29	+
5	1.5/1.0	80	4.25	6.21	–
6[d]	1.5/1.0	80	4.51	7.42	++
7[e]	1.5/1.0	25	4.16	6.45	–

Reagents and conditions: The post-cured COPNA(PR,TPA) resin (post-cured at 300 °C for 1 h) 2.5 g, fuming sulfuric acid (15 wt% SO_3) 20 mL, 15 h, N_2

[a] Determined by titration

[b] Rate constant for the esterification of acetic acid with EtOH

[c] Solubility to boiling water: (insoluble) < + < ++ < +++ (partially soluble)

[d] Without post-curing

[e] Time 24 h

The results for the sulfonation of the post-cured COPNA(PR,TPA) resin by sulfuric acid are shown in Table 2. When the reaction was conducted at 150 °C, k was smaller than that of 80 °C in spite of the higher acid density (entries 1 and 2). We considered that the approach of substrates might be difficult with the decrease of hydrophobic nature of the catalyst by the introduction of the hydrophilic SO_3H group. The reaction at 80 °C resulted in the production of the insoluble S-COPNA resin with the large rate constant ($k = 5.97 \times 10^{-4}$) (entry 2). Sulfonation of the post-cured COPNA resin with TPA/PR = 1.0/1.0 was performed, but the S-COPNA resin was partially soluble to boiling water (entry 4). When the post-cured COPNA resin was treated with chlorosulfonic acid at 25 °C in dichloromethane [20, 22, 34], the S-COPNA resin was partially soluble to boiling water (entry 5). Although the rate constant ($k = 5.97 \times 10^{-4}$) of the S-COPNA resin sulfonated by sulfuric acid was slightly smaller than that by fuming sulfuric acid ($k = 6.45 \times 10^{-4}$), we adopted the S-COPNA(PR,TPA) resin sulfonated by sulfuric acid for further evaluation because of the low price of sulfuric acid (Table 1, entry 7 and Table 2, entry 2). It was insoluble to boiling water and many hot organic solvents such as benzene, THF, chloroform, ethanol, acetone, EtOAc, CH_3CN, DMF, and DMSO. The plausible structural model of the S-COPNA(PR,TPA) resin was shown in Fig. 1. The essential feature of the model is characterized by the triarlymethane structure and some amounts of the unreactive aldehydes. The IR spectrum showed the characteristic absorption at 1686 cm^{-1} due to the CHO group and 1168 and 1033 cm^{-1} due to the SO_3H group. The benzene ring with the CHO group would not be sulfonated by sulfuric acid, since *p*-methylbenzaldehyde did not react with sulfuric acid at 80 °C for 15 h under nitrogen.

In order to lead to the S-COPNA(NP,TPA) resin (TPA/NP = 1.5/1.0) (NP = naphthalene), we attempted the preparation of the COPNA(NP,TPA) resin. The mixture of NP, TPA, 5 wt% of TsOH was heated at 180 °C for 14 h under nitrogen, but the reaction did not occur.

Table 2 Sulfonation of the post-cured COPNA(PR,TPA) resin by sulfuric acid

Entry	TPA/PR	Temp (°C)	Acid density (mmol g^{-1})[a]	$k^{b} \times 10^{-4}$	Solubility[c]
1	1.5/1.0	150	4.93	3.28	–
2	1.5/1.0	80	3.85	5.97	–
3[d]	1.5/1.0	25	3.51	5.39	–
4	1.0/1.0	80	5.06	8.18	+
5[d, e]	1.5/1.0	25	4.19	6.27	+

Reagents and conditions: The post-cured COPNA(PR,TPA) resin (post-cured at 300 °C for 1 h) 2.5 g, sulfuric acid 20 mL, 15 h, N_2

[a] Determined by titration

[b] Rate constant for the esterification of acetic acid with EtOH

[c] Solubility to boiling water: (insoluble) < + < ++ < +++ (partially soluble)

[d] Time 24 h

[e] Sulfonated by chlorosulfonic acid

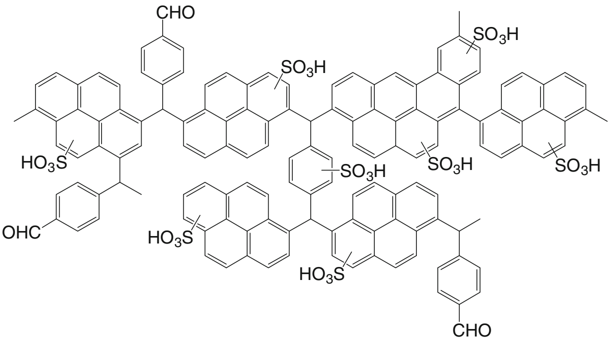

Fig. 1 Schematic model of the S-COPNA(PR,TPA) resin

Synthesis of the S-COPNA(PR,BA) resin

Next, we investigated the synthesis of S-COPNA(PR,BA) resin. The mixture of PR, BA, and TsOH (5 wt% of [PR + BA]) was heated at 160 °C for 1.5 h under nitrogen to give the B-stage resin [8]. The melt was heated at 300 °C for 1 h under nitrogen to give the less hard black solid compared to the post-cured COPNA(PR,TPA) resin [8].

The post-cured COPNA(PR,BA) resin was converted into the S-COPNA(PR, BA) resins by fuming sulfuric acid (15 wt% SO_3) or sulfuric acid at 80 °C for 15 h under nitrogen (Table 3). However, the S-COPNA resins were soluble or partially soluble to hot water.

An attempt to cross-link the chain of the COPNA(PR,BA) resin by a small amount of TPA was carried out. The post-cured COPNA(PR,BA/TPA) resin was prepared by heating the mixture of PR, BA, TPA, and 5 wt% of TsOH at 160 °C for 2 h under nitrogen followed by heating at 300 °C for 1 h. Sulfonation of the resin by

Table 3 Sulfonation of the post-cured COPNA(PR,BA) resin by fuming sulfuric acid or sulfuric acid

Entry	BA/PR	Acid density (mmol g^{-1})[a]	$k^b \times 10^{-4}$	Solubility[c]
1[d]	1.0/1.0	–	–	Soluble
2[d]	1.5/1.0	5.41	9.04	+++
3	1.0/1.0	–	–	Soluble
4	1.5/1.0	0.64	2.32	++

Reagents and conditions: The post-cured COPNA(PR,BA) resin (post-cured at 300 °C for 1 h) 2.5 g, sulfuric acid 20 mL, 80 °C, 15 h, N_2

[a] Determined by titration

[b] Rate constant for the esterification of acetic acid with EtOH

[c] Solubility to boiling water: (insoluble) < + < ++ < +++ (partially soluble)

[d] Sulfonated by fuming sulfuric acid (15 wt% SO_3) 20 mL

Table 4 Sulfonation of the post-cured COPNA(PR,BA/TPA) resin by sulfuric acid

Entry	BA/TPA/PR	Temp (°C)	Acid density (mmol g^{-1})[a]	$k^{b} \times 10^{-4}$	Solubility[c]
1	0.8/0.2/1.0	150	4.55	4.48	++
2	0.8/0.2/1.0	80	1.76	4.20	–
3	0.9/0.1/1.0	80	1.16	3.53	–
4[d]	0.8/0.2/1.0	25	0.57	1.99	–
5[d, e]	0.8/0.2/1.0	25	4.95	7.90	++

Reagents and conditions: The post-cured COPNA(PR,BA/TPA) resin (post-cured at 300 °C for 1 h) 2.5 g, sulfuric acid 20 mL, 15 h, N_2

[a] Determined by titration

[b] Rate constant for the esterification of acetic acid with EtOH

[c] Solubility to boiling water: - (insoluble) < + < ++ < +++ (partially soluble)

[d] Time 24 h

[e] Sulfonated by fuming sulfuric acid (15 wt% SO_3) 20 mL

sulfuric acid was conducted and the results are shown in Table 4. Addition of a small amount of TPA was effective for the synthesis of the insoluble S-COPNA resins (entries 2–4). The rate constant ($k = 4.20 \times 10^{-4}$) of the S-COPNA resin (BA/TPA/PR = 0.8/0.2/1.0) was larger than that of the S-COPNA resin (BA/TPA/PR = 0.9/0.1/1.0) ($k = 3.53 \times 10^{-4}$) (entries 2 and 3). Sulfonation by fuming sulfuric acid led to the S-COPNA resin with the highest rate constant ($k = 7.90 \times 10^{-4}$), however, it was partially soluble to boiling water (entry 5). We employed the S-COPNA(PR,BA/TPA) resin (BA/TPA/PR = 0.8/0.2/1.0) sulfonated by sulfuric acid at 80 °C for further evaluation. It was insoluble to boiling water and many hot organic solvents such as benzene, THF, chloroform, ethanol, acetone, EtOAc, CH_3CN, DMF, and DMSO.

In order to lead to the S-COPNA(NP,BA) resin (BA/NP = 1.0/1.0), we made an attempt to prepare the COPNA(NP,BA) resin. The mixture of NP, BA, 5 wt% of TsOH was heated at 180 °C for 14 h under nitrogen, but the reaction did not proceed.

Evaluation of the S-COPNA resins

The analytical data and catalytic activities of the S-COPNA(PR,TPA) and S-COPNA(PR,BA/TPA) resins were shown in Table 5 together with those of the S-COPNA(PR,PXG) and S-COPNA(NP,PXG) resins sulfonated by chlorosulfonic acid. This S-COPNA(PR,PXG) resin possessed the highest activity in the S-COPNA resins which we prepared previously [9]. However, sulfonation by chlorosulfonic acid required the complex experimental procedure for the exclusion of a large amount of the adsorbed chlorosulfonic acid. We improved the experimental procedure for the exclusion of adsorbed chlorosulfonic acid. The obtained S-COPNA resins were refined via the conversion to sodium salt by addition of

Table 5 Analytical data and catalytic activities of the S-COPNA resins

Entry	Catalyst	Chemical composition	SO_3H (mmol g^{-1})[a]	Acid density (mmol·g^{-1})[b]	$k^c \times 10^{-4}$
1	S-COPNA (PR,TPA)	$CH_{0.576}O_{0.268}S_{0.027}$	1.52	3.85	5.97
2	S-COPNA (PR,BA/TPA)	$CH_{0.575}O_{0.119}S_{0.010}$	0.67	1.76	4.20
3	S-COPNA (PR,PXG)[d]	$CH_{0.671}O_{0.312}S_{0.086}$	4.21	5.04	8.59
4	S-COPNA (NP,PXG)[d]	$CH_{0.649}O_{0.365}S_{0.086}$	4.04	4.21	4.74

[a] Calculated from chemical composition

[b] Determined by titration

[c] Rate constant for the esterification of acetic acid with EtOH

[d] Sulfonated by chlorosulfonic acid

NaOH solution followed by acidification and heating the powder of the S-COPNA resins at 150 °C for 3 h. A large amount of the sulfate ion formed from the hydrolysis of adsorbed chlorosulfonic acid was detected by sulfate test paper.

It is noteworthy that high rate constants were realized in the S-COPNA(PR,TPA) and S-COPNA(PR,BA/TPA) resins in spite of their lower degree of sulfonation. It might be due to the increase of hydrophobic nature of the catalyst by less hydrophilic CHO groups in place of terminal CH_2OH groups in the S-COPNA(PR,PXG) and S-COPNA(NP,PXG) resins. In every case, acid densities of the

Table 6 Recycle experiments of the formation of ethyl acetate catalyzed by the S-COPNA resins

Cycle	First	Second	Third	Fourth	Fifth
S-COPNA(PR,TPA), 4 h Conv. (%)[a]	88	87	86	86	86
S-COPNA(PR,BA/TPA), 4 h Conv. (%)[a]	76	60	55	49	46
S-COPNA(PR,PXG),[b] 4 h Conv. (%)[a]	92	89	90	89	90
S-COPNA(NP,PXG),[b] 4 h Conv. (%)[a]	82	81	82	84	84

Reagents and conditions: EtOH (1.0 mol), CH_3COOH (0.1 mol), catalyst (200 mg), 80 °C, 4 h

[a] Determined by titration

[b] Sulfonated by chlorosulfonic acid

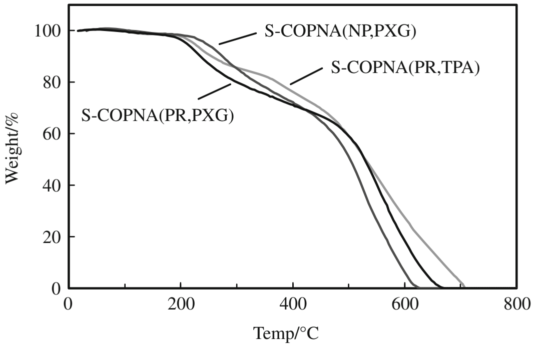

Fig. 2 TGA curves of the S-COPNA resins in air

Table 7 Rate constants for various reactions

Catalyst	CH_3COOH + EtOH ($\times 10^{-4}$ mol dm^3 min^{-1})[a]	PhCOOH + EtOH ($\times 10^{-5}$ mol dm^3 min^{-1})[b]	CyOAc + H_2O ($\times 10^{-4}$ mol dm^3 min^{-1})[c]	OleOAc + H_2O ($\times 10^{-5}$ mol dm^3 min^{-1})[d]
S-COPNA (PR,TPA)	5.97	2.24	5.71	2.61
S-COPNA (PR,PXG)[e]	8.59	3.68	6.00	1.20
S-COPNA (NP,PXG)[e]	4.74	0.99	3.27	0.21
Mordenite	0.11	0.00	0.04	0.15
Montmorillonite K10	1.63	0.00	0.03	0.00
Nafion NR50	0.56	0.00	0.25	0.00
Nafion SAC-13	0.79	0.00	0.15	0.00
Amberlyst 15	2.33	0.00	0.26	0.08
Sulfuric acid	46.00	15.50	0.80	1.00

[a] Reagents and conditions: EtOH (1.0 mol), CH_3COOH (0.1 mol), catalyst (200 mg), 80 °C

[b] Reagents and conditions: EtOH (1.0 mol), PhCOOH (0.1 mol), catalyst (200 mg), 80 °C

[c] Reagents and conditions: CyOAc (4.4 mmol), H_2O (3.3 mol), catalyst (200 mg), 90 °C

[d] Reagents and conditions: OleOAc (4.4 mmol), H_2O (3.3 mol), catalyst (200 mg), 100 °C

[e] Sulfonated by chlorosulfonic acid

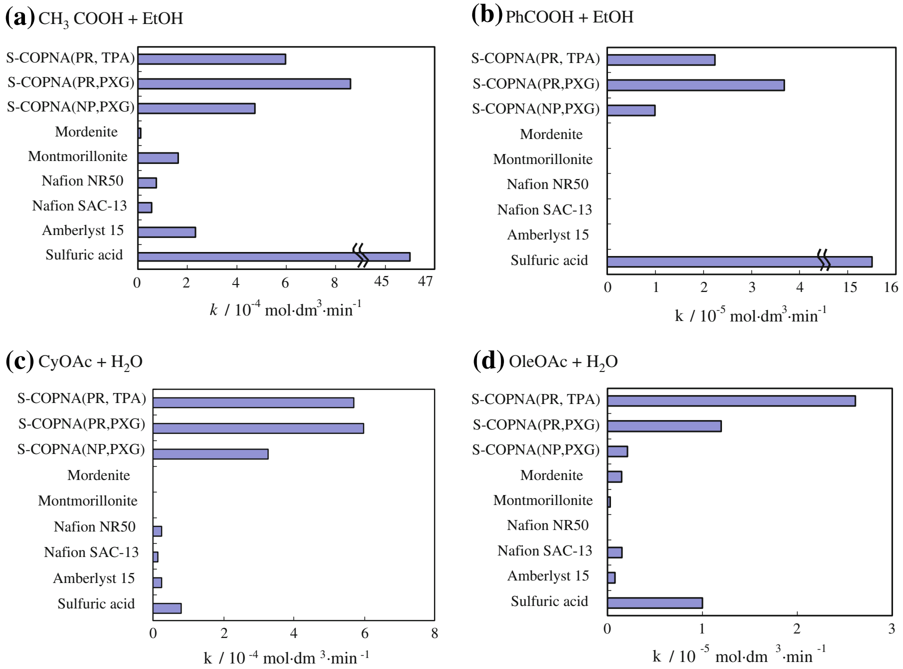

Fig. 3 Acid-catalyzed liquid-phase reactions: **a** Rate constants for the formation of ethyl acetate (80 °C). **b** Rate constants for the formation of ethyl benzoate (80 °C). **c** Rate constants for the hydrolysis of cyclohexyl acetate (90 °C). **d** Rate constants for the hydrolysis of oleyl acetate (100 °C)

sulfonated resins determined by titration were larger than degree of sulfonation. Especially, there were large differences in the S-COPNA(PR,TPA) and S-COPNA(PR,BA/TPA) resins prepared by the reaction with sulfuric acid (entries 1 and 2). It will be because of containing weakly acidic functional groups such as phenolic hydroxyl groups. However, it was difficult to discuss the detailed structure of the sulfonated resins at the present time.

In order to check the reusability of the catalysts, the catalysts were removed by decantation and employed for the next experiment. The S-COPNA(PR,TPA) resin was reused without significant loss of activities (Table 6). On the other hand, the activities of the S-COPNA(PR,BA/TPA) resin decreased gradually.

The thermal stability of the S-COPNA resins was evaluated by thermogravimetric analysis (TGA) in air atmosphere (Fig. 2). After an initial weight loss due to evaporation of absorbed water, the two-step decomposition process was observed for all polymers. For the S-COPNA(PR,TPA), the S-COPNA(PR,PXG), and S-COPNA(NP,PXG) resins, decomposition reactions started at around 200, 190, and 220 °C. Heating these polymers above around 470, 480, and 460 °C resulted in a rapid decrease in weight, respectively. In view of the thermostability, the S-COPNA(PR,TPA) resin was somewhat superior to the S-COPNA(PR,PXG) resin.

Rate constants of the S-COPNA(PR,TPA), S-COPNA(PR,PXG), and S-COPNA(NP,PXG) resins for esterification of carboxylic acids and the hydrolysis of esters were summarized in Table 7. Figure 3a shows the rate constants for the formation of ethyl acetate (80 °C) on the S-COPNA resins (200 mg). The S-COPNA(PR,TPA) resin was less active than the S-COPNA(PR,PXG) resin, but still exhibited higher activities than conventional solid acids such as mordenite, Montmorillonite K10, Nafion NR50, Nafion SAC-13, and Amberlyst 15. The S-COPNA(PR,TPA) resin showed the high activity for the formation of ethyl benzoate (80 °C), while conventional solid acids were inert for the reaction (Fig. 3b). For the hydrolysis of cyclohexyl acetate, the activity of the S-COPNA(PR,TPA) resin was almost equal to that of S-COPNA(PR,PXG) resin, and considerably higher than those of the other acidic catalysts including sulfuric acid (Fig. 3c). It is noteworthy that the activity of the S-COPNA(PR,TPA) resin was higher than that of the S-COPNA(PR,PXG) resin for the hydrolysis of oleyl acetate in spite of the lower degree of sulfonation (Fig. 3d). This is probably because of the increase of hydrophobic nature of the catalyst by less hydrophilic CHO groups in place of terminal CH_2OH groups in the S-COPNA(PR,PXG) resin [35, 36].

Conclusions

We synthesized the S-COPNA resins cross-linked by aromatic aldehydes and evaluated the performance as strong protonic acids. Interestingly, these S-COPNA resins were highly active in spite of lower degree of sulfonation. The S-COPNA(PR,TPA) resin was reused without significant loss of activities, and exhibited the higher performance than conventional solid acids.

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