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Synthesis of the sulfonated condensed polynuclear aromatic (S-COPNA) resins as strong protonic acids

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ABSTRACT

The mixture (PXG/PR=1.00) of pyrene (PR) and *p*-xylylene glycol (1,4-benzenedimethanol) (PXG) in the presence of 5 wt % of *p*-toluenesulfonic acid (TsOH) was heated at 140 °C for 45 min under nitrogen to give the highly viscous condensed polynuclear aromatic (COPNA) resin. It was converted into an infusible and insoluble solid by further heating at 300 °C for 1 h. The obtained material was treated with fuming sulfuric acid at 80 °C for 15 h under nitrogen to give the sulfonated COPNA resin. The similar acidic resin was prepared by the reaction of phenanthrene or naphthalene with PXG in the presence of TsOH followed by sulfonation. The performance of the sulfonated polymers as the strong protonic acids was evaluated.

1. Introduction

Sulfonated polymers have attracted considerable attention for a wide range of potential usefulness as solid acid catalysts, conductive polymers, and materials for making fuel cell membranes.[1] Cation exchange resins, such as Amberlyte are superior acid catalysts easy to synthesize, however, these polymers cannot be employed at high temperature. Nafion-H is typically used as the polymeric superacid, however, it is difficult to synthesize and its acid activity is low. Recently, the sugar catalyst, which was a new class of sulfonated carbons derived from incomplete carbonization and sulfonation of simple sugars, has been devised.[2,3] Sulfonated poly(1,4-diphenoxyphenylene)[4] and sulfonated carbon material derived from polynuclear aromatic compounds, such as naphthalene,[5] have been prepared. The advantage utilizing polynuclear aromatic compounds as the starting material is that sulfonated polymers with various substituents can be designed.

Otani et al. have reported the synthesis of the condensed polynuclear aromatic (COPNA) resins with extremely high thermostability through the dehydration reaction between fused aromatic hydrocarbons (Aro) and *p*-xylylene glycol (1,4-benzenedimethanol) (PXG) catalyzed by *p*-toluenesulfonic acid (TsOH).[6–10]

These results prompted us to study the synthesis of the sulfonated COPNA (S-COPNA) resins. The obtained materials were quite insoluble to boiling water and many hot organic solvents. Furthermore, these can be employed at high temperature and showed high acid activities. In this paper, we wish to report the synthesis and evaluation of the S-COPNA resins.

2. Results and discussions

2.1. Synthesis of the S-COPNA resins

First, synthesis of the S-COPNA(PR) resin (PXG/PR=1.25 in the molar ratio) (PR=pyrene) was investigated as the model case. By Otani's method,[6] the mixture of pyrene, PXG, and *p*-TsOH (5 wt % of [PXG+PR]) was heated at 140 °C for 45 min under nitrogen to give a highly viscous yellow melt (called as a B-stage resin). The melt was converted into an infusible and insoluble black solid by subsequent post-curing at 300 °C for 1 h under nitrogen.

The post-cured COPNA(PR) resin was sulfonated by fuming sulfuric acid (15 wt % SO_3) at 80 °C for 15 h under nitrogen to give the S-COPNA(PR) resin as the black powder (Table 1, entry 2). The plausible structural model of the S-COPNA(PR) resin was shown in Fig. 1. 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. Although sulfonation at 150 °C afforded the material with the highest acid density, k was smaller than that of 80 °C (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

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Table 1
Sulfonation of the post-cured COPNA(PR) resin by fuming sulfuric acid[a]

Entry	Temp (°C)	Time (h)	Acid density (mmol g^{-1})[b]	$k^c\times10^{-4}$	Solubility[d]
1	150	15	6.01	4.63	+
2	80	15	5.12	6.59	–
3	25	24	4.44	5.43	–
4[e]	150	15	5.70	3.66	–
5[e]	80	15	4.44	3.44	–
6[e]	25	24	0.30	0.63	–

[a] Reagents and conditions: the post-cured COPNA(PR) resin (PXG/PR=1.25 in the molar ratio, post-cured at 300 °C for 1 h) 2.5 g, fuming sulfuric acid (15 wt % SO_3) 20 mL, N_2.
[b] Determined by titration.
[c] Rate constant for the esterification of acetic acid with EtOH.
[d] Solubility to boiling water: –(insoluble)<+<++(partially soluble).
[e] Sulfuric acid (20 mL) was used.

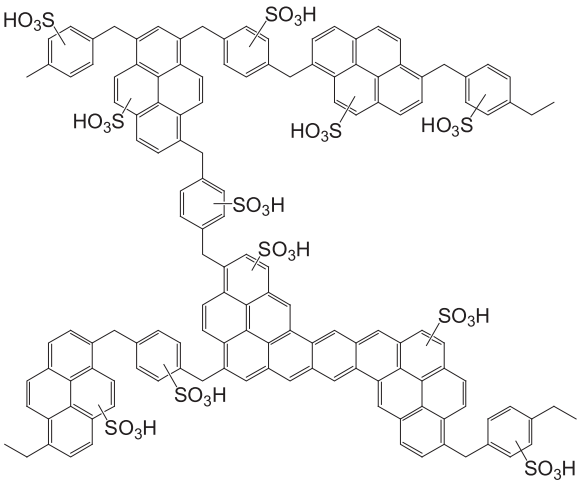

Fig. 1. Schematic model of the S-COPNA(PR) resin.

introduction of the hydrophilic SO_3H group. In addition, it was partially soluble to boiling water. When sulfonation was carried out by concentrated sulfuric acid, rate constants were smaller than those by fuming sulfuric acid (entries 4–6). It is interesting to note that the rate constant (k=5.43×10^{-4}) of the material sulfonated by fuming sulfuric acid at 25 °C was larger than that by concentrated sulfuric acid at 80 °C (k=3.44×10^{-4}) in spite of the same acid density (4.44 mmol g^{-1}) (entries 3 and 5). The S-COPNA(PR) resin obtained by the reaction at 80 °C in fuming sulfuric acid was the most active material (entry 2).

Table 2 summarizes the results for sulfonation of the post-cured COPNA(PR) resins with various molar ratios PXG/PR. We chose the post-cured COPNA(PR) resins with PXG/PR=1.00, 1.25, and 1.50, which were suitable for the formation of the B-stage resin.[6] The best result was obtained by the sulfonation of the post-cured COPNA resin with PXG/PR=1.00 (entry 1).

The influence of post-curing temperature on the activity of the S-COPNA resin was explored (Table 3, entries 1–4). When the COPNA(PR) resin without post-curing was treated with fuming sulfuric acid, a color change from yellow to black was observed, suggesting that aromatization of the carbon skeleton may occur during sulfonation. Although the obtained resin possessed the highest activity, it required long time to filter the precipitate and the sedimentation in water was slow (entry 4). Post-curing, especially at 300 °C, was effective for quick filtration and fast sedimentation (entry 2). Sulfonation of the COPNA(PR) resin with and without post-curing by $ClSO_3H$ in dichloromethane gave the S-COPNA(PR) resins with high activities (entries 5–7). The color change of the precipitate from brown to black during work-up, especially heating at 150 °C, was observed. However, it was difficult to exclude adsorbed chlorosulfonic acid. Therefore, complex experimental procedures were required.

Table 2
Sulfonation of the post-cured COPNA(PR) resins with various molar ratios by fuming sulfuric acid[a]

Entry	PXG/PR	Acid density (mmol g^{-1})[b]	$k^c\times10^{-4}$	Solubility[d]
1	1.00	5.18	7.08	–
2	1.25	5.12	6.59	–
3	1.50	4.67	5.08	–

[a] Reagents and conditions: the post-cured COPNA(PR) resin (post-cured at 300 °C for 1 h) 2.5 g, fuming sulfuric acid (15 wt % SO_3) 20 mL, 80 °C, 15 h, N_2.
[b] Determined by titration.
[c] Rate constant for the esterification of acetic acid with EtOH.
[d] Solubility to boiling water: –(insoluble) <+<++(partially soluble).

Table 3
Sulfonation of the COPNA(PR) resins treated at various curing temperature by fuming sulfuric acid[a]

Entry	Curing temp (°C)	Temp (°C)	Acid density (mmol g^{-1})[b]	$k^c\times10^{-4}$	Solubility[d]
1	400	80	4.96	6.98	–
2	300	80	5.18	7.08	–
3	200	80	5.51	7.84	–
4	none	80	5.33	8.56	–
5[e]	400	25	4.93	7.98	+
6[e]	300	25	5.04	8.59	–
7[e]	none	25	5.23	9.35	++

[a] Reagents and conditions: the COPNA(PR) resin (PXG/PR=1.00 in the molar ratio) 2.5 g, fuming sulfuric acid (15 wt % SO_3) 20 mL, 15 h, N_2.
[b] Determined by titration.
[c] Rate constant for the esterification of acetic acid with EtOH.
[d] Solubility to boiling water: –(insoluble) <+<++(partially soluble).
[e] Sulfonated by chlorosulfonic acid in dichloromethane.

Table 4 shows the analytical data and catalytic activities of the S-COPNA(PR) resins synthesized by the different sulfonating agents. Rate constants were correlated with the degree of sulfonation calculated from chemical composition. Acid densities of the sulfonated resins determined by titration were larger than the degree of sulfonation. Especially, there was a large difference in the sulfonated resin prepared by the reaction with sulfuric acid (entry 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, since IR spectra of the S-COPNA(PR) resin prepared by the sulfonation with sulfuric acid was almost the same as the others except for the appearance of the new absorption at 1560 cm^{-1} due to the benzene ring.

Next, we prepared the post-cured COPNA resins consisting of the other condensed polynuclear aromatic structure. The results are shown in Table 5. The post-cured COPNA(PH) (PH=phenanthrene) and the COPNA(NP) (NP=naphthalene) resins were prepared in good yields by the similar procedure with the post-cured COPNA(PR) resin (curing temp 300 °C) (entries 2 and 5). Attempts to prepare the COPNA(AT) (AT=anthracene) resin failed because the mixture of PXG, anthracene, and 5 wt % of TsOH did not make the uniform melt even at 260 °C because of the high melting point of anthracene (218 °C)[11] (entries 3 and 4). Table 6 shows the results for the sulfonation of the various post-cured COPNA resins by fuming sulfuric acid. Although sulfonation of the post-cured COPNA(PH) resin at 150 °C gave the solid with higher acid density, the activity was lower than that of the solid sulfonated at 80 °C (entries 2 and 3). In addition, it was partially soluble to boiling water. Sulfonation at 80 °C led to the most active material (entry 3). The rate constant (k=6.22×10^{-4}) of the S-COPNA(PH) resin was smaller than that of the S-COPNA(PR) resin (k=7.08×10^{-4}) (entries 1 and 3). Similarly, the S-COPNA(NP) resin was obtained by the sulfonation of the post-cured COPNA(NP) resin at 150 °C (entry 5). The rate constant (k=4.87×10^{-4}) of the S-COPNA(NP) resin was smaller than those of the S-COPNA(PR) and the S-COPNA(PH) resins. The obtained S-COPNA resins were insoluble to boiling water and many hot