SUPPLEMENTAL MATERIALS

Synthesis of Cyclohexene Carbonate Catalyzed by Polymer-supported Catalysts

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The preparation of catalysts comprise the following steps: (1) the introduction of connecting arms; (2) the graft of ligand; (3) the coordination of zinc chloride. In this work, a series of PS supported metal salt catalysts were prepared by introducing connecting arms with different lengths. The preparation procedure is illustrated in Scheme S1.

M= Fe、Co、Ni、Zn;

X=Cl⁻、Br⁻、CH₃COO⁻;

n = 0~15; a = 1, 2, 3; b = 1, 2, 3。

Scheme S1 Preparation procedure of the catalysts

The introduction of connecting arms

PS (0.02mol, calculated according to the chlorine content, 3g) was swelled in toluene for 24 h. Then ethylene glycol (0.11mol, 6mL), anhydrous potassium carbonate (5g, 0.04mol), tetrabutyl ammonium bromide (0.01mol, 1g) were added. After stirring and refluxing for **24h**, the reaction mixture was filtered and washed with ethanol. The obtained product was extracted with toluene for 12h followed by drying in vacuum at 60°C till weights became constant. Then the modified PS was obtained, named PS-EG. The procedures for the introduction of other connecting arms were similar. And a series of modified PS with different lengths connecting arms were prepared by using diethylene glycol, triethylene glycol and polyethylene glycol (PEG200, PEG 300, PEG 400, PEG 600) instead of ethylene glycol, named PS-DEG, PS-TEG, PS-PEG200, PS-PEG300, PS-PEG400 and PS-PEG600, respectively. FT-IR and surface properties studies were performed to characterize PS and the above modified PS. The FT-IR spectra were shown in Figure S1. The BET surface areas and pore structure results were given in Table S1.

Figure S1. FT-IR spectra of PS, PS-EG, PS-DEG, PS-TEG, PS-PEG200, PS-PEG300, PS-PEG400 and PS-PEG600.

As shown in Figure S1, the FT-IR spectras of PS, PS-EG, PS-DEG, PS-TEG, PS-PEG200, PS-PEG300, PS-PEG400 and PS-PEG600 were similar in addition to the emergence of some new peaks. This indicated that the structure of PS was well retained. In the FT-IR spectrum of PS-EG, the band around 3450cm^{-1} was due to $-\text{OH}$ group stretching vibration. The bands at 2924cm^{-1} and 2852cm^{-1} can be assigned to C-H asymmetric stretching vibration and stretching vibration. The peaks at 1612 , 1584 , 1508 , and 1467cm^{-1} were related to the C=C bond vibration absorption peak of benzene ring. The band around 1384cm^{-1} was due to primary alcohol $-\text{CH}_2\text{OH}$ groups stretching vibration. The band around 1101cm^{-1} , which was due to C-O-C bond typical stretching vibration, also appeared in the FT-IR spectra of PS-DEG, PS-TEG, PS-PEG200, PS-PEG300, PS-PEG400 and PS-PEG600, and it became stronger with the $-\text{CH}_2\text{CH}_2\text{O}-$ group increasing. Meanwhile, the peak intensity of C-Cl ($\sim 670\text{cm}^{-1}$) in each of the spectra of the modified PS was significantly weaker after the introduction of connecting arms. These results indicated that the connecting arms were introduced succesfully.

Table S1 The BET surface areas and pore structure of PS and modified PS

Entry	modified PS	BET surface area ($\text{m}^2\cdot\text{g}^{-1}$)	Pore volume ($\text{cm}^3\cdot\text{g}^{-1}$)	Pore diameter (nm)
1	PS	77.59	0.2109	10.87
2	PS-EG	45.58	0.1606	14.09
3	PS-DEG	47.28	0.1657	14.02
4	PS-TEG	49.97	0.1729	13.84
5	PS-PEG200	60.21	0.1820	12.09
6	PS-PEG300	62.68	0.1888	12.05
7	PS-PEG400	68.94	0.2085	12.10

The graft of ligand

Taking PS-PEG200 as an example, the modified PS was swelled in toluene for 24 h. Then thionyl chloride (0.028mol, 2mL) was added. After stirring at 80°C for 10h, the reaction mixture was filtered and washed with ethanol. The product was obtained after drying in vacuum at 60°C till weights became constant and named PS-PEG200-Cl. FT-IR study was performed and the spectrum was shown in Figure S2.

After the above product was swelled in toluene for 24 h, 2-aminopyridine (0.04mol, 3.8g) and anhydrous potassium carbonate (5g, 0.04mol) were added. The reaction mixture was filtered and washed with ethanol after stirring and refluxing for several hours. The product named PS-PEG200-2ap was obtained after drying in vacuum at 60°C till weights became constant. The procedures of ligand grafting for other modified PS were similar. The FT-IR spectra was shown in Figure S2.

Figure S2. FT-IR spectra of PS, PS-PEG200, PS-PEG200-Cl and PS-PEG200-2ap.

As shown in Figure S2, the –OH group stretching vibration ($\sim 3450\text{cm}^{-1}$) in the spectrum of PS-PEG200 became stronger comparing with that in the spectra of PS while it was significantly weaker in the spectrum of PS-PEG200-Cl. This indicated that partial hydroxyl groups were replaced by –Cl. The characteristic absorption peaks of pyridine ring appeared at 1580cm^{-1} . The band around 1350cm^{-1} was due to C-N stretching vibration. The peaks at 750cm^{-1} and 1650cm^{-1} could be assigned to N-H out-of-plane bending vibration and in-plane bending vibration. The results showed that 2-aminopyridine had been grafted onto the carrier.

The coordination of zinc chloride

After the products of the previous step were swelled in toluene (0.47mol, 50mL) for 24 h, zinc chloride (0.037mol, 5g), acetone (0.069mol, 5mL) were added. After stirring and refluxing for a certain time, the reaction mixture was filtered and washed with ethanol. Then the obtained catalysts were dried in vacuum at 60°C till weights became constant. The contents of metal elements were determined by icp-aes and the results were given in Table S2.

Table S2 The contents of metal elements

Entry	Catalysts	contents of metal elements (W%)
1	PS-2ap-ZnCl ₂	13.1
2	PS-EG-2ap-ZnCl ₂	13.7
3	PS-DEG-2ap-ZnCl ₂	12.9
4	PS-TEG-2ap-ZnCl ₂	12.1
5	PS-PEG200-2ap-ZnCl ₂	13.4
6	PS-PEG300-2ap-ZnCl ₂	13.3

7	PS-PEG400-2ap-ZnCl ₂	13.1
8	PS-PEG600-2ap-ZnCl ₂	13.2

The morphology of the samples was observed by scanning electron microscopy (SEM) (JEOL JSM-7500F). As shown in Figure S3, PS has a plain surface (Figure S3 (a)). However, there is a roughening of surface (Figure S3 (b)) to be observed with the coordinating of zinc chloride on the materials.

Figure S3. SEM images of PS (a) and PS-DEG-2ap-ZnCl₂ (b).

Thermogravimetric-differential scanning calorimetry (TG-DSC) analysis (from 20 to 650 °C) of samples was performed in N₂ flow on a NETZSCH-STA-409 PC equipment (Figure S4). The results indicate that the PS-DEG-2ap-ZnCl₂ is stable up to 200 °C, and the slight weight loss may be due to the loss of physisorbed water. There are two endothermic peaks, one at 330 °C and the other at 450 °C, attributable to the decomposition of the graft copolymer and polymer support, respectively. The results clearly demonstrate that the catalyst is stable in air and is thermally stable up to 200 °C.

Figure S4. TG and DSC curves of PS-DEG-2ap-ZnCl₂ .

Characterization of cyclohexene carbonate

The product of the cycloaddition reaction of cyclohexene oxide with CO₂ was characterized by IR, ¹H NMR, ¹³C NMR and GC/MS. And the results were shown in Figure S5, Figure S6, Figure S7.

Figure S5. FT-IR spectra of cyclohexene carbonate.

As shown in Figure S5, the bands at 2944cm⁻¹ and 2869 cm⁻¹ can be assigned to C-H asymmetric stretching vibration and stretching vibration. The peak at approximately 1796 cm⁻¹ was related to the C=O vibration absorption. The band around 1168cm⁻¹ was due to C-O-C stretching vibration.

Figure S6. The ^1H , ^{13}C NMR spectra of cyclohexene carbonate.

Figure S6 showed the ^1H , ^{13}C NMR spectra of cyclohexene carbonate. As illustrated by the NMR spectra, there was no split for the 2C, 7C ($\delta = 75.78$ ppm) and 2H, 7H (4.654–4.703 ppm), which indicated that 2C, 7C and 2H, 7H were in the same chemical environment. It is the obvious evidence which proves the *cis* product was obtained.

Figure S7. Mass spectra of cyclohexene carbonate.