Polymer 143 (2018) 87-95

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Hypercrosslinked porous polycarbazoles from carbazolyl-bearing aldehydes or ketones

Rong-Rong Zhang ^{a, b}, Qing Yin ^b, Hai-Peng Liang ^b, Qi Chen ^{b, ***}, Wei-Hua Luo ^{a, **}, Bao-Hang Han ^{b, *}

^a Department of Chemical Engineering and Technology, Central South University of Forestry and Technology, Changsha, 410004, China ^b CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing, 100190, China

ARTICLE INFO

Article history: Received 7 December 2017 Received in revised form 18 March 2018 Accepted 27 March 2018 Available online 29 March 2018

Keywords: Carbazole Carbonyl group Friedel–crafts reaction Oxidative coupling polymerization Hypercrosslinked polymers Porosity

ABSTRACT

Hypercrosslinked polymers have drawn increasing interest due to their porous structure, large specific surface area, and excellent chemical and thermal stability. Using the carbonyl bearing carbazole monomers **Cz-22-27**, a series of hypercrosslinked porous polycarbazoles **CPOP-22-27** have been synthesized through oxidative coupling polymerization and Friedel–Crafts reaction in one-step promoted by FeCl₃. The Brunauer–Emmett–Teller specific surface areas of **CPOP-22-27** are between 440 and 760 m² g⁻¹. Their dominant pore sizes vary from 0.99 to 1.06 nm, which indicating that the polymers are predominantly microporous. This work provides a new method to synthesis of hypercrosslinked porous polycarbazoles from carbonyl functionalized carbazoles. It is also found that parts of aldehyde groups can not react through the Friedel–Crafts alkylation when increasing the number of carbazole groups. The residual aldehyde groups in the polymer can even react with Tollens' reagent solution to form Ag nanoparticles composite.

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1. Introduction

Hypercrosslinked polymers (HCPs) [1–3] have been reported in earlier time and known as one category of porous organic polymers (POPs) [4,5]. These porous polymers with high surface area and good chemo/thermal stability have shown wide applications as catalyst supports [6–9], gas storage materials [10–13], separation [14], and purification matrix [15,16]. HCPs are usually prepared with low cost methods and cheap raw materials. Up to now, Lewis acid catalyzing Friedel–Crafts alkylation is one of the most used template-free methods to prepare HCPs with high Brunauer–Emmett–Teller (BET) specific surface area [17–20]. Using suitable monomers and linkers, different types of hypercrosslinked porous polymers can be synthesized. In some cases, monomer and linker can be designed as a single monomer [21–23]. Therefore, synthesis of HCPs with this method exhibits high efficiency and flexibility.

FeCl₃-catalyzed oxidative coupling polymerization is a costeffective approach to prepare porous polycarbazoles firstly reported by our group [24,25]. Through this simple and convenient method, we and other groups have developed a series of porous conjugated polycarbazoles [26,27], which show potential use in selective gas storage [24], organic photocatalysis [28,29], heterogeneous transformation [30], and catalyst encapsulation [31]. FeCl₃, as an oxidant and Lewis acid, can be the catalyst for both oxidative coupling polymerization and Friedel–Crafts reaction [32–34]. Therefore, we have designed and synthesized vinyl or hydroxymethyl bearing carbazole derivatives to prepare hypercrosslinked porous polycarbazoles through Friedel–Crafts reaction and oxidative coupling polymerization in one-step using FeCl₃ as catalyst [22].

As we know, aldehyde and ketone are also the suitable substrates for the Friedel–Crafts alkylation [32]. In order to develop new hypercrosslinked porous polycarbazoles and explore facile synthetic methods, herein, a series of carbazole-based hypercrosslinked porous polymers have been synthesized via Friedel–Crafts reaction and oxidative coupling polymerization in one-step catalyzed by FeCl₃ from carbazolyl-bearing aldehydes or





^{*} Corresponding author.

^{**} Corresponding author.

^{***} Corresponding author.

E-mail addresses: chenq@nanoctr.cn (Q. Chen), lwh6803@163.com (W.-H. Luo), hanbh@nanoctr.cn (B.-H. Han).

ketones under refluxing conditions or room temperature. Monomers with different structures were designed to tune the porosities of the obtained porous materials. Moreover, as to the porous polymer prepared from aldehyde derivatives, Ag nanoparticles can be loaded into the material by the chemical reduction in situ of the Tollens' reagent [35–37]. We think it is a facile approach to prepare HCPs supported metal nanoparticle composite materials.

2. Experimental section

2.1. Materials

Carbazole (98.0 wt%, Adamas), 1,4-dibromobenzene (98.0 wt%, Adamas), 4-acetylphenylboronic acid (97 + wt%, Adamas), 4bromo-2,6-difluorobenzylaldehyde (98 + wt%, Adamas), 1-(4bromo-2,6-difluorophenyl)ethenone (97.0 wt%, Innochem), 4fluoroacetophenone (98.0 wt%, Innochem), 4-fluorobenzaldehyde (98.0)wt%. Alfa), 1-(4-bromo-2,6-difluorophenyl)ethenone (97.0 wt%, Ark), 3,5-dibromobenzaldehyde (98.0 wt%, Ark), dis (triphenylphosphine)palladium (II) dichloride (99.9 wt%, Acros), Iron (III) chloride anhydrous (98.0 wt%, Adamas), and silver nitrate (98.9 wt%, Alfa) were purchased from the corresponding companies. Ammonia, potassium carbonate (99.0 + wt%), 1,10phenanthroline (98 wt%), copper iodide (99.9 wt%), potassium tert-butoxide (98.0 wt%), and tetrakis (triphenylphosphine) palladium (0) (99.9 wt%) were ordered from Aladdin Industrial Corporation, Shanghai. N, N-Dimethylformamide (DMF), petroleum ether (PE), dichloromethane (DCM), methanol, 1,2-dichloroethane (DCE), and tetrahydrofuran (THF) are of analytically pure and were obtained from Beijing Chemical Reagents Company. Ultrapure water (18 M Ω cm) was produced by a Millipore-ELIX water purification system. All the other chemical reagents and solvents were commercially available. 4-(9H-9-Carbazolyl)phenylboronic acid, and 9-(4-bromophenyl)-9H-carbazole were synthesized according to the reported procedure [26]. Cz-22 was prepared following the reported procedure [30]. Carbon dioxide (99.5%), methane (99.999%), and nitrogen (99.999%) were purchased from Haike Yuanchang Gas Company.

2.2. Structural characterization and instrumental analysis

The detail information was shown in the Supporting Information.

2.3. Synthesis of Cz-23

To a two-neck flask were added 9-(4-bromophenyl)-9H-carbazole (0.58 g, 1.8 mmol), 4-acetylphenylboronic acid (0.42 g, 2.8 mmol), and aqueous potassium carbonate solution (8.0 mL, 2.0 M) in THF (10.0 mL). The mixture was degassed by the freeze--pump-thaw cycle two times. Pd(PPh₃)₄ (104.01 mg, 0.09 mmol) was added and degassed by freeze-pump-thaw once again. The white solution was slowly heated to 80 °C with nitrogen protection and kept for 48 h and then extracted with DCM and water. The organic layers were combined and dried with anhydrous Na₂SO₄. The crude product was concentrated under reduced pressure and further purified by silica gel column chromatography (PE/DCM = 1/6-1/3) to produce the desired compound (0.38 g, 60.3%). ¹H NMR $(400 \text{ MHz}, \text{ CDCl}_3) \delta 10.13 \text{ (s, 1H)}, 8.19 \text{ (d, } J = 7.7 \text{ Hz}, 2\text{H}), 8.05 \text{ (d,}$ J = 8.1 Hz, 2H), 7.90 (t, J = 7.1 Hz, 4H), 7.73 (d, J = 8.3 Hz, 2H), 7.49 (dd, J = 16.8, 7.6 Hz, 4H), 7.34 (t, J = 7.3 Hz, 2H).¹³C NMR (100 MHz, CDCl3) & 191.0, 145.3, 139.8, 137.8, 137.3, 134.6, 129.6, 128.0, 126.8, 126.6, 125.2, 122.7, 119.6, 119.4, 108.9. MS (EI-TOF) m/z: calculated for C₂₅H₁₇NO: 347.13 [M]; found: 347 [M].

2.4. Synthesis of Cz-24

To a two-neck flask were added 4-(9H-9-Carbazole)phenylboronic acid (1.52 g, 5.3 mmol). 4-bromo-2.6difluorobenzylaldehyde (0.77 g, 3.5 mmol), THF (20.0 mL), and aqueous potassium carbonate solution (12.5 mL, 2.0 M). The mixture was degassed by the freeze-pump-thaw cycle two times. Pd(PPh₃)₂Cl₂ (280.4 mg, 0.4 mmol) was added and degassed by freeze-pump-thaw once again. Then the bright yellow solution was slowly heated to 80 °C under nitrogen atmosphere and kept for 48 h and then extracted with DCM and water. The organic layers were combined and dried with anhydrous Na₂SO₄. Finally, the crude product was concentrated under reduced pressure and further purified by silica gel column chromatography (PE/DCM = 1/4-1/2) to furnish the desired product **Cz-24** (1.25 g, 93.0%). ¹H NMR $(400 \text{ MHz}, \text{ CDCl}_3) \delta$ 10.43 (s, 1H), 8.19 (d, J = 7.7 Hz, 2H), 7.85 (d, J = 8.5 Hz, 2H), 7.75 (d, J = 8.5 Hz, 2H), 7.48 (dt, J = 8.1, 7.5 Hz, 4H), 7.38–7.32 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 184.2, 164.9, 162.3, 148.6, 140.5, 139.3, 136.1, 128.6, 127.6, 126.2, 123.7, 120.4, 112.8, 110.7, 109.7. MS (EI-TOF) m/z: calculated for C₂₅H₁₅F₂NO: 383.11 [M]; found: 383 [M].

2.5. Synthesis of Cz-25

The monomer **Cz-25** was synthesized in the yield of 74.1% following the similar procedure of the monomer **Cz-22** using 4-fluoroacetophenone as reagent. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.5 Hz, 2H), 8.18 (d, *J* = 7.7 Hz, 1H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.53–7.44 (m, 2H), 7.38–7.33 (m, 1H), 2.73 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 197.0, 142.2, 140.2, 135.5, 130.1, 126.5, 126.2, 123.8, 120.6, 120.5, 109.8, 26.7. MS (EI-TOF) *m/z*: calculated for C₂₀H₁₅NO: 285.12 [M]; found: 285 [M].

2.6. Synthesis of Cz-26

The monomer **Cz-26** was synthesized in the yield of 82.0% following the similar procedure of the monomer **Cz-24** using 4-bromo-2,6-difluorobenzylaldehyde as reagent. ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 7.7 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.47 (ddd, *J* = 9.8, 9.3, 4.5 Hz, 4H), 7.35 (dd, *J* = 11.4, 4.8 Hz, 4H), 2.70 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 194.3, 162.0, 159.5, 145.4, 140.6, 138.8, 136.6, 128.5, 127.5, 126.1, 123.6, 120.4, 110.8, 110.5, 109.7, 32.6. MS (EI-TOF) *m/z*: calculated for C₂₆H₁₇F₂NO: 397.13 [M]; found: 397 [M].

2.7. Synthesis of Cz-27

To a two-neck flask were added carbazole (1.93 g, 11.5 mmol), 3,5-dibromobenzaldehyde (1.33 g, 5.1 mmol), DMF (20.0 mL), potassium carbonate (2.88 g, 20.9 mmol), 1,10-phenanthroline (0.23 g, 1.2 mmol), and copper iodide (2.02 g, 10.6 mmol). The solution was kept stirring under nitrogen atmosphere for 10 min at room temperature and then 120 °C for 24 h. Ice water (50.0 mL) was poured to quench the reaction. The gray green crude product was filtrated, washed with water and dried. The resulting solid was obtained by further purification via silica gel column chromatography (PE/ DCM = 2/1) to give **Cz-27** (1.31 g, 59.0%). ¹H NMR (400 MHz, CDCl₃) δ 10.22 (s, 1H), 8.23 (s, 2H), 8.17 (d, *J* = 7.7 Hz, 3H), 8.12 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 4H), 7.47 (t, *J* = 7.3 Hz, 4H), 7.35 (t, *J* = 7.0 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 191.1, 141.3, 140.9, 140.2, 131.2, 127.1, 126.8, 124.6, 121.6, 121.3, 110.1. MS (MALDI-TOF) *m/z*: calculated for C₃₁H₂₀N₂O: 436.16 [M]; found: 436.3 [M].

2.8. Synthesis of CPOP-22–27

Polymers CPOP-22~27 can be synthesized from the corresponding monomers Cz-22~27 via FeCl3-promoted reaction individually. The detail procedure of preparing CPOP-22 from monomer **Cz-22** is given as follows. Under nitrogen atmosphere. Cz-22 (0.09 g, 0.33 mmol) was dissolved in anhydrous DCE (10.0 mL). The mixture was added dropwise through a constantpressure drop funnel to the solution of anhydrous ferric chloride (1.30 g, 8.25 mmol) in anhydrous DCE (20.0 mL). The mixture was kept stirring for 48 h at 80 °C, and then methanol (50.0 mL) was added to quench the polymerization. The crude polymer was filtered and washed with methanol, water, and THF. The asprepared polymer **CPOP-22** was further purified with boiling methanol for 24 h and then with THF for another 24 h in a Soxhlet extractor and dried in a vacuum oven at 110 °C overnight (99% in yield). Following the similar procedure, polymers CPOP-23 and CPOP-24 were obtained with yields 89% and 96%, respectively. CPOP-25 (yield 98%) and CPOP-26 (yield 96%) were obtained from the monomers Cz-25 and Cz-26 at room temperature polymerization, respectively. For CPOP-27, it was obtained from the monomer Cz-27 at room temperature in DCM with yield of 82%.

2.9. Preparation of AgNPs/CPOP-27 composite

Procedure for preparation of **AgNPs/CPOP-27** composite was according to the improved method [38]. Dilute ammonia (0.5%) was

added dropwise to a mixture of silver nitrate (0.20 g, 1.12 mmol) and deionized water (10.0 mL) to form a yellow precipitate. The fresh Tollens' reagent can be obtained after the dissolving of the yellow precipitation. **CPOP-27** (0.25 g, 0.57 mmol) was then added to the freshly prepared Tollens' reagent solution immediately. The mixture was kept stirring at 45 °C for 24 h out of the light. A yellow solid of 0.26 g was obtained after filtrating, washing with ethanol and water, and drying in vacuum oven at 45 °C for 24 h.

2.10. Catalytic reduction of 4-nitrophenol (4-NP) by AgNPs/CPOP-27 composite

In order to measure the catalytic activity of **AgNPs/CPOP-27** composite, the reduction of 4-NP was performed in quartz cuvette (1 cm of optical path, volume 4 mL), and the sodium borohydride (NaBH₄) was used as a reductant. In the experiment, 4-NP (1.44 mM, 0.10 mL) was added to the quartz cuvette followed by treated with the freshly prepared aqueous NaBH₄ solution (6.87 mM, 2.80 mL). **AgNPs/CPOP-27** composite (1.0 mg/mL, 0.10 mL) dispersed well in deionized water was dropped to the mixed solution mentioned above. The reducing progress is monitored and recorded by UV–vis spectra with the absorbance ranging from 244 to 600 nm and defined time intervals at room temperature. (The catalytic reduction reaction should be carried out within a few minutes after the solution was prepared so as to minimize the decomposition of NaBH₄.)



Scheme 1. Preparation of the monomers Cz-22~27.



Scheme 2. Preparation of the hypercrosslinked polycarbazoles CPOP-22~27.



Fig. 1. ¹³C CP/MAS NMR spectra of CPOP-22, CPOP-26, and CPOP-27.



Fig. 2. (a) Nitrogen adsorption–desorption isotherms of **CPOP-22-27** measured at 77 K, the adsorption and desorption branches are labeled with solid and open symbols, respectively. (For clarity, the isotherms of **CPOP-23-27** were shifted vertically by 105, 295, 215, 60, and 75 cm³ g⁻¹, respectively.) (b) The PSD profiles of **CPOP-22-27** calculated by NLDFT.

3. Results and discussion

A series of carbazolyl-bearing aldehydes or ketones Cz-22~26 (Scheme 1) were synthesized as monomers by classical N-arylation and Suzuki coupling reaction, respectively. All the monomers were well characterized with ¹H NMR, ¹³C NMR, and MS. It has been reported that the number of carbazolyl group in the monomer plays important roles in permanent porosity of porous polycarbazoles via FeCl₃-promoted oxidative coupling reaction [26,39]. Furthermore, we also prepared the monomer Cz-27 to investigate effects on the chemical structure and porosity of the corresponding hypercrosslinked polycarbazole. For these monomers, carbazole moieties can either be linked each other by FeCl₃-promoted oxidative coupling reaction, or coupled with aldehyde or ketone groups by FeCl₃-catalyzed Friedel-Crafts alkylation. Therefore, the corresponding hypercrosslinked polycarbazoles CPOP-22~27 (shown in Scheme 2) were synthesized through Friedel–Crafts reaction/ oxidative coupling polymerization in one-step using FeCl3 as catalytic reagent.

All the hypercrosslinked polycarbazoles are characterized by ¹³C CP/MAS NMR. The spectra of CPOP-22, CPOP-26, and CPOP-27 were illustrated as representative examples (see Fig. 1). For CPOP-22, the main resonance signals are located at about 139, 124, 110, and 53 ppm. Generally, the signal peak at 139 ppm corresponds to the phenyl carbons linking with nitrogen atom. High intensity peak of 124 ppm is attributed to the signal peak of other substituted phenyl carbons. The unsubstituted phenyl carbons are located at 110 ppm. These three signal peaks are derived from the polycarbazole networks consistent with previous reports [26,27]. The tertiary methylene carbons linked with phenyl and carbazole are located at 53 ppm. For CPOP-26, besides the main resonance signals mentioned above, the peak at 159 ppm is belonged to the phenyl carbons bonding with fluorine atom. The peak of methyl carbon was located at 32 ppm. The ¹³C CP/MAS NMR spectra for the other obtained polymers are shown in Fig. S1 (Supporting Information), which appear with similar resonance intensity to CPOP-22 and CPOP-26. From all the spectra, we can see a new broad peak at 53 ppm ascribed to the tertiary carbon methylene carbons linked with phenyl and carbazole. Meanwhile, the carbon signals of

Polymers	$S_{\rm BET}^{a} (m^2 g^{-1})$	S_{micro}^{b} (m ² g ⁻¹)	V_{total}^{c} (cm ³ g ⁻¹)	$D_{\rm pore}^{\rm d}({\rm nm})$	CO ₂ uptake ^e (wt%)	CH ₄ uptake ^e (wt%)
CPOP-22	440	313	0.24	1.06	6.91	1.07
CPOP-23	760	552	0.45	0.99	9.78	1.44
CPOP-24	750	575	0.62	1.02	9.13	1.33
CPOP-25	755	545	0.42	0.99	9.76	1.23
CPOP-26	530	464	0.31	1.06	9.34	1.52
CPOP-27	674	408	0.29	1.04	6.96	1.18

Porosity properties and gas uptake capacities of polymers.

^a Specific surface area calculated from the nitrogen adsorption isotherm using the BET method.

^b Micropore surface area calculated from the adsorption branch of the nitrogen adsorption–desorption isotherm using the *t*-plot method.

^c Total pore volume at $P/P_0 = 0.99$.

^d Date calculated from nitrogen adsorption isotherms with the NLDFT method.

^e Date were obtained at 1.0 bar and 273 K.

monomer aldehyde or ketone group (190–180 ppm) almost disappeared except for **CPOP-27**. These results prove that the Friedel–Crafts reaction with aldehyde or ketone group takes place definitely. Furthermore, the competition consists in the Friedel–Crafts alkylation of aldehyde groups and oxidative coupling reaction of carbazole group. For **CPOP-27**, we can see that the peak belonging to the aldehyde carbon is also located clearly at 191 ppm after polymerization, indicating that a part of aldehyde groups have not reacted through Friedel–Crafts alkylation due to competition of more carbazole groups in the oxidative coupling reaction.

Based on the comparison of FTIR spectra from monomers and polymers (Fig. S2, Supporting Information), we can find the strong

signals at about 1700 cm⁻¹ of monomer aldehyde or ketone group become weaker after polymerization. The result can also prove that the aldehyde or ketone group participate the Friedel–Crafts reaction during the polymerization. The thermal stabilities of all the polymers are characterized by TGA via heating the sample to 800 °C at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere (Fig. S3, Supporting Information). TGA plot shows that there still have about 70% mass residues even when the temperature rises to 800 °C (calculation based on the weight of materials after removing adsorbed water at temperature above 100 °C) and the decomposition temperature of the polymers is about 400–500 °C, indicating the good thermal stability of obtained polymers.

A series of polymers were synthesized from monomers with



Scheme 3. Preparation of AgNPs/CPOP-27 composite.

Table 1



Fig. 3. TEM images of AgNPs/CPOP-27 composite in different reaction time: (a) 12 h; (b) 24 h; (c) 48 h; (d) the corresponding EDX of AgNPs/CPOP-27 composite.

various structures to not only establish the methodology but also tune the porosity such as BET specific surface area, PSD, and pore volume. For porous organic polymers with irregular pore structures, porosity tuning is mainly affected by the monomer structure and preparative method [40,41]. To investigate the porosity of the polymers CPOP-22~27, the nitrogen adsorption-desorption testing was conducted. As shown in Fig. 2a, the materials display the formation of the model I combined with II sorption isotherms according to the IUPAC classification [42]. A sharp increase at the relative pressure (P/P_0) under 0.05 indicates permanent microporous nature of the obtained polymers. The other sharp increase at high relative strain above 0.90 can indicate the macroporous property. Hysteresis can be observed apparently in the entire scope of the relative strain. The BET specific surface areas of CPOP-22~27 calculated from 0.01 to 0.10 (P/P_0) are ranged from 440 to 760 $m^2 g^{-1}$. From the adsorption branch of the isotherms, the PSD profiles of the polymers can be obtained using the NLDFT approach. As shown in Fig. 2b, the primary pore sizes of CPOP-22~27 vary from 0.99 to 1.06 nm.

The absorbing ability of **CPOP-22~27** for methane and carbon dioxide were measured at 273 K. Figs. S4 (Supporting Information), and S5 (Supporting Information) show the methane and carbon dioxide adsorption isotherms. The carbon dioxide capture capacities range from 6.91 to 9.78 wt% and the methane capture capacities vary from 1.07 to 1.52 wt%, which indicate that the uptake performance of all the obtained materials are at a moderate level. The key porosity parameters of **CPOP-22~27** are listed in Table 1, including the BET specific surface area, micropore surface area, pore volume, dominant pore size, and gas uptake performance.

CPOP-27 containing aldehyde groups even can be used as the supporting matrices for loading AgNPs via further redox reaction with Tollens' reagent (Scheme 3). **CPOP-27** was added to the freshly prepared Tollens' reagent solution at 45 °C and the mixture was stirred for 24 h under dark condition, the desired product was

filtered and washed with plenty of water to remove the soluble impurities. To explore the formation and related morphology of **AgNPs/CPOP-27** composite, TEM images of **AgNPs/CPOP-27** composite in different reaction time are shown in Fig. 3 (a–d). We can see the **AgNPs** gradually grows and the related particle sizes become apparently larger from 2 to 10 nm (8 h) to 5–20 nm (24 h) with the reaction time. The corresponding EDX technique suggests that AgNPs are embedded in the **CPOP-27** successfully (Fig. 3d). TGA data in Fig. S6 (Supporting Information) also indicate the actual loading capacity of AgNPs is about 2.0 wt % via heating the sample to 800 °C at a heating rate of 10 °C min⁻¹ under air atmosphere.

The BET specific surface area of the AgNPs/CPOP-27 composite is not obviously changed with compared to CPOP-27. Both of CPOPand AgNPs/CPOP-27 display 27 similar nitrogen adsorption-desorption isotherm and PSD profile. The assynthesized AgNPs/CPOP-27 composite shows microporous features and its dominant PSD are mainly located around 0.53, 0.73, and 1.26 nm based on NLDFT method shown in Fig. 4. The AgNPs encapsulated in the porous polymer can be utilized as catalyst for the catalytic transformation in the pharmaceuticals and agrochemical [43]. The AgNPs loaded on the polymer show good catalytic activity in reduction, which can be used for the conversion of nitro compound precursors or intermediates to the corresponding amino or amine compounds. The catalytic activity of AgNPs/CPOP-27 composite was examined by the reduction of 4-NP to 4aminophenol (4-AP) at room temperature with slightly excess NaBH₄ as reducing reagent [44]. We can easily distinguish the process of catalytic reaction by the color change of solution from yellow to colorless gradually. Both the reactant and product can be monitored by UV-vis spectroscopy without any detectable byproduct. Fig. S7a (Supporting Information) depicts the timevarying catalytic reaction performance of 4-NP with the existence of AgNPs/CPOP-27. The absorption peak of 4-nitrophenolate ions at 400 nm decreased gradually accompanied by the rising up of 4-AP



Fig. 4. Nitrogen adsorption-desorption isotherm of AgNPs/CPOP-27 measured at 77 K and its PSD profile calculated by NLDFT.

peak at about 300 nm. The disappearing of the peak of 4-NP is attributed to consumption of the substrate and results in the fading of solution. The generation of 4-AP led to the emergence of the peak at about 300 nm. After 1100 s, peak at 400 nm almost disappeared, suggesting the complete conversion of 4-NP to 4-AP. The kinetic process of 4-NP reduction is considered to be pseudo-first-order [45]. The dependence of $\ln (c_t/c_0)$ on time with NaBH₄ as reductant and AgNPs/CPOP-27 as catalyst is shown in Fig. S7b (Supporting Information). There is obviously linear relationship consistented to the pseudo-first-order kinetics between $\ln (c_t/c_0)$ and reaction time. As the first-order rate constant, the value of kabout **AgNPs/CPOP-27** composite is 0.277 min^{-1} ($4.62 \times 10^{-3} \text{ s}^{-1}$) from the slope of curve in Fig. S7b (Supporting Information). Usually, to judge the activity of the catalyst, the active factor k_a ($k_a = k/k_a$ *m*, *m* is the total mass of catalyst) is considered as the better way [46]. As reported, the k_a of the Ag–NP/C composites is 1.69 s⁻¹ g⁻¹ [47], the Fe₃O₄@SiO₂-Ag nanocomposite is 7.76 s⁻¹ g⁻¹ [48], and the Ag/N-RGO is $7.4 \text{ s}^{-1} \text{ g}^{-1}$ [49]. These are all lower than $46.2 \text{ s}^{-1} \text{ g}^{-1}$ of **AgNPs/CPOP-27** composite prepared in this work. The high catalytic activity is ascribed to the in situ synthesized AgNPs dispersed well in high specific surface area of porous polymer, which can produce more potential catalytic sites to promote the interaction of AgNPs with 4-NP, reaching the better catalytic effect.

4. Conclusions

In summary, a series of hypercrosslinked porous polycarbazoles CPOP-22~27 have been successfully synthesized via FeCl3-promoted one-step Friedel-Crafts alkylation and oxidative coupling reaction from the carbonyl group functionalized carbazole monomers Cz-22~27. The BET specific surface areas of obtained materials range from 440 to 760 m² g⁻¹. The pore size distribution analysis indicates that the polymers are predominantly microporous and mesoporous. The uptake capacity of CPOP-22~27 for methane and carbon dioxide at 273 K were measured at a moderate level. Due to the competition between the Friedel–Crafts alkylation of aldehyde groups and oxidative coupling reaction of carbazole groups, parts of aldehyde groups could not react through the Friedel-Crafts alkylation when increasing the number of carbazole groups. Therefore, more residual aldehyde groups in CPOP-27 were found than in other polymers. The residual aldehyde groups in the polymer can react with Tollens' reagent solution to form Ag nanoparticles composite, which is a facile method to prepare HCP/AgNPs composite for catalytic reduction.

Acknowledgements

The financial support of the National Science Foundation of China Grants (21574031 and 21574032) and the Sino-German Center for Research Promotion (Grant GZ1286) is acknowledged.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.polymer.2018.03.062.

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