Hierarcal porous polystyrene-based activated carbon spheres for CO₂ capture

Xiaoxia Ren

Taiyuan University of Technology

Changming Zhang (✉ zhangchangming@tyut.edu.cn)

Taiyuan University of Technology

Lifang Kou

Taiyuan University of Technology

Rongxian Wang

Taiyuan University of Technology

Yaqi Wang

Taiyuan University of Technology

Rui Li

Taiyuan University of Technology

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Abstract

Activated carbon spheres with high specific surface area and hierarcal porous texture were prepared from polystyrene-based macroreticular resin spheres by air pre-oxidization and steam activation. The as-prepared carbon spheres had a specific surface area of $1274.95 \text{ m}^2 \text{ g}^{-1}$, total pore volume of $1.09 \text{ cm}^3 \text{ g}^{-1}$ and micropore volume of $0.47 \text{ cm}^3 \text{ g}^{-1}$. Moreover, these carbon spheres showed a hierarcal porous texture composed of ultrafine micropores (0.5-1 nm), micropores (1–2 nm), mesopores (10–50 nm) and macropores (50–100 nm). A CO_2 adsorption capacity of 2.82 mmol g^{-1} for carbon spheres can be obtained at 30°C and 1 atm. Further, after introducing nitrogen-containing functional groups by gaseous ammonia at 600°C , these carbon spheres exhibited a high CO_2 adsorption capacity of 3.2 mmol g^{-1} . In addition, excellent cyclic stability, low hygroscopicity and regenerability temperature suggested these carbon spheres were favorable for CO_2 capture.

Introduction

Global climate warming has been the most significant environmental issue for human being in 21st century. Since CO_2 exhaust from power plants is considered as a major greenhouse gas causing climate change, great efforts have been devoted to develop the new materials and technologies for CO_2 capture to reduce the amount of CO_2 released into the atmosphere in the past decade. In this case, various methods for CO_2 capture such as membrane separation (Xie et al., 2019; Liu et al., 2019; Ma et al., 2020), solvent absorption (Lv et al., 2015; Chen et al., 2016; Shen et al., 2016; Gusnawan et al., 2020; Gusnawan et al., 2020), and adsorption (Ahmed et al., 2020; Chan et al., 2017; Singh et al., 2021; Varghese et al., 2020) have been widely investigated. Among these methods, adsorption based on solid sorbents is considered as one of the most potential approaches due to its low cost and energy consumption.

Over the past decade, solid sorbents such as zeolites (Azmi et al., 2019; Ammendola et al., 2019), porous silicas (Guo et al., 2015; Guo et al., 2017), porous aluminas (Sakwanovak et al., 2011; Gunathilake et al., 2016), metal-organic frameworks (Ding et al., 2019; Yu et al., 2017) and porous carbons (Creamer et al., 2016; Guo et al., 2020; Yang et al., 2017) have been extensively explored for CO_2 capture. However, the adsorption capacity of CO_2 on zeolites and porous silicas would be reduced sharply in the presence of water which is inevitable in flue gas, limiting its applied spaces. In addition, porous aluminas and metal-organic frameworks have exhibited low CO_2 capture capacity. It is worth noting that porous carbons have many unique physicochemical properties such as high specific surface area, large pore volume, good hydrophobic interface, and high chemical and thermal stability, which not only can provide high CO_2 capture capacity, but also high capacity retention in the presence of water.

The main influence factors of porous carbons on CO_2 capture are consisted of specific surface area, surface functional groups and pore structure. Theoretically, high specific surface area of porous carbons can provide large physical adsorption spaces for CO_2 due to small molecular size of CO_2 ($\sim 0.33 \text{ nm}$). Surface functional groups, especially nitrogen-containing functional groups, strengthen adsorption

capacities of CO₂ on porous carbons by chemical binding. Pore structures provide diffusion pathways and adsorption spaces of CO₂. However, only low adsorption capacities of CO₂ on porous carbons can be obtained due to the complex pore structures such as the size distribution, tortuosity, and shape of the pores, etc, although porous carbons have high specific surface area (Olivares-Marín et al., 2011; Zhang et al., 2010). These cases are especially notable in atmospheric pressure (~ 1 atm), suggesting that reasonable pore structures play an important role in the adsorption of CO₂ on porous carbons. In addition, to further improve the CO₂ adsorption capacities of porous carbons, nitrogen species are introduced into porous carbons through various methods including impregnation (Kassab et al., 2012; Wang et al., 2012), grafting (Liu et al., 2011; Pevida et al., 2008). Impregnating amines onto porous carbons often suffer from the reduction of pore volume and instability. Alternatively, grafting nitrogen species onto porous carbons by gaseous ammonias at high temperature can avoid the decrease of pore volume on the maximum extent, as well as small amine content is fit for CO₂ desorption completely.

Although porous carbons have many excellent physicochemical properties, powdered porous carbons are easy to blow away, low loading density and recycling difficulty, which restrict its industrial application. In this case, many special shape porous carbons such as activated carbon fibers (Shen et al., 2011), carbon monoliths (Zhao et al., 2017; Querejeta et al., 2017) and spherical activated carbons (Uddin et al., 2020; Sun et al., 2013) have been prepared successfully to be used as CO₂ solid sorbents. Among these solid sorbents, spherical activated carbons have high compressive strength, high bulk density, excellent mobility and low pressure drop, being fit for large scale fluidized beds. Unfortunately, only a very few studies have been devoted to use spherical activated carbons for CO₂ capture.

Herein, an attempt to prepare hierarchical porous carbon spheres by air pre-oxidizing and steam activating polystyrene-based macroreticular resin spheres is carried in this work. The resulting carbon spheres combine macroporous cores as CO₂-buffering reservoirs, mesoporous wall with smaller CO₂ diffusion resistance, and micropores for CO₂ adsorption. Our method and products have several novel characteristics over other techniques and products. First of all, carbon spheres prepared by the method have high specific surface area ($> 1200 \text{ m}^2 \text{ g}^{-1}$), and hierarchical porous structure composed of micropores, mesopores and macropores, providing high adsorption capacities and fast adsorption rates for CO₂. Second, the synthetic process finished only by a facile pre-oxidation and activation, is simple and easy operational, and the precursors of carbon spheres, macroreticular resin spheres, are commercially available, which is favorable for industrial production. Third, the as-prepared carbon spheres have large size (0.3-1.0 mm), high mechanical strength ($8\text{--}12 \text{ N cm}^{-2}$) and loading density (0.42 g cm^{-3}), which facilitate its industrial application for CO₂ capture. The experimental results exhibit high adsorption capacities of CO₂ on the carbon spheres as the solid sorbent.

Experimental Section

Carbon spheres preparation

The preparation of carbon spheres was carried out by means of air pre-oxidization and steam activation for which polystyrene-based macroreticular resin spheres (commercial purchase from Nankai Co. Ltd of Tianjin, China) were chosen as carbon precursors. In a typical experiment, the polystyrene-based macroreticular resin spheres labeled as PSRSs were firstly air pre-oxidized from room temperature to 300 °C at a heating rate of 0.3 °C min⁻¹, and kept 4 h at 300 °C. Further, the oxidized resin spheres (OPSRs) were heated up to 810 °C at a rate of 3 °C min⁻¹ and then maintained at this temperature to activate for 2 h by steam at a flow rate of 120 mL min⁻¹, thus carbon spheres labeled as PSRCSs were obtained.

To obtain the nitrogen-containing carbon spheres, The as-prepared PSRCSs were treated with gaseous ammonia under a flow rate of 50 ml min⁻¹ for 4 h at 600 °C in a vertical tube furnace. The obtained sample was labeled as NPSRCSs.

Characterization

The morphologies of PSRSs and PSRCSs were analyzed by field emission scanning electron microscopy (FESEM) (JEOL-JSM6360, Japan) at an accelerating voltage of 10 kV. The specific surface area and pore structure of PSRSs, PSRCSs and NPSRCSs were characterized by N₂ adsorption/desorption isotherms at 77 K (Micromeritics ASAP-2020). Specific surface area was obtained using Brunauer-Emmett-Teller (BET) method. Pore size distribution was calculated by the density functional theory (DFT) method. The total pore volume (V_{total}) was calculated at the relative pressure of 0.99. Crystalline structure of PSRSs, PSRCSs and NPSRCSs were analyzed by X-ray power diffraction (XRD) (Philips X'pert diffractometer with CuK α_1 radiation (λ = 1.5418 Å)). C, H, N, O contents were analyzed by using an element analyzer (Elementar vario EL CUBE). X-ray photoelectron spectroscopy (XPS) characterization was carried out in an ESCALAB 250 instrument with 150 W Al K α probe beam to analyze nitrogen species of NPSRCSs. N1s envelopes were fitted into Gaussian-Lorentzian component profiles using CasaXPS software.

CO₂ adsorption

The CO₂ adsorption and desorption performance of these sorbents was measured in a thermogravimetric analyzer (SETSYS EVOLUTION TGA 16/18). Prior to the CO₂ adsorption experiments, the adsorbents were heated up to 120 °C at a rate of 10 °C min⁻¹ in a nitrogen flow of 50 ml min⁻¹, and kept at 120 °C for 1 h to remove physically adsorbed substances. Afterwards, the samples were cooled to 30 °C. Further, the N₂ flow was switched to a pure CO₂ flow or mixture flow containing CO₂ and H₂O for adsorption at 1 atm. The samples were kept 30 °C for 60 min and finally the gas flow was switched to N₂ to regenerate the samples. The volume fraction of H₂O in mixture flow was determined by its fraction of saturated vapor pressure of H₂O in designated temperature and total pressure.

Results And Discussion

Photograph and SEM images of PSRSs and PSRCSs are presented in Fig. 1. Large quantities of bright PSRCSs prepared by the method can be obtained (Fig. 1a). The particle diameter distribution of PSRCSs

is in the range of 0.3-1.0 mm, which is almost normal distribution (Fig. 1b). Further, it can be seen from Fig. 1c that PSRSs have a good sphericity and smooth surface. After steam activation for 120 min, the outer surface of PSRCS becomes rough, as shown in Fig. 1e, resulting from the etching of steam to carbon at high temperature, which is similar with the previous reported works (Liu et al., 2019). In addition, the cross section of PSRSs exist some mesopores and macropores (Fig. 1d). These pores are mainly slit structure produced during sphere forming. More obviously, after steam activation, developed mesopores and reduced macropores can be observed in the cross section of PSRCSs (Fig. 1f). The explanation is that steam can intercalate easily into inner of PSRSs and further etch the mesopore structures accompanying with the production of some micropores (Ren et al., 2020). On the other hand, reduced macropores can be attributed to the shrinkage of C-C skeleton during carbonization at high temperature (Nakagawa et al., 1999).

The nitrogen adsorption-desorption isotherms (as seen in Fig. 2a) for PSRSs and PSRCSs are essentially of type IV with pronounced H3-type hysteresis loops, being characteristic of the mesoporous materials being comprised of agglomerated pores with broad pore size distribution. At a lower relative pressure, there is a steep rise in both isotherms, indicating the presence of some micropores. Moreover, along with steam activation, N_2 adsorption capacity for PSRCSs increases remarkably, suggesting that large quantity of micropores have been introduced into PSRCSs. In addition, at high relative pressure (0.8-0.99), hysteresis loops of mesopores are steep considerably, indicating large mesopore structure closing to macropores existed in the PSRSs and PSRCSs (Zhu et al., 20014). Fig. 2b shows DFT pore size distribution for PSRSs and PSRCSs. The peaks for both samples appear mainly at <2 nm, and 10-100 nm, that is, PSRSs and PSRCSs exhibit hierarcal porous structure composed of micropores (<2 nm) for CO_2 adsorption, mesopores (10-50 nm) providing fast CO_2 diffusion pathways and macropores (50-100 nm) as CO_2 -buffering reservoirs. It is worth noting that PSRCSs have abundant ultrafine micropores at the range from 0.5 to 0.6 nm compared with PSRSs, this make it a potential adsorbent candidate.

Table 1 summarizes the porous texture parameters and elemental components of all samples. The BET surface area, total pore volume and micropore volume of PSRCSs after steam activation for 120 min are up to $1274.95 \text{ m}^2 \text{ g}^{-1}$, $1.09 \text{ cm}^3 \text{ g}^{-1}$ and $0.47 \text{ cm}^3 \text{ g}^{-1}$, respectively, a highly developed porous structure. Further, after gaseous ammonia treatment, the specific surface area of NPSRCSs drops only by 6%, indicating gaseous ammonia treatment does not have a serious detrimental effect on pore structure of PSRCSs. Noticeably, a high bulk density of 0.42 g cm^{-3} for PSRCSs and NPSRCSs facilitates the improvement of volume adsorption capacities of CO_2 , compared with the low bulk density of other carbon material such as powered activated carbons (Wang et al., 2019) and common activated carbon fibers (Lee et al., 2013). In addition, only a low nitrogen content of 0.66 wt% for PSRCSs can be obtained by activation at high temperature, due to the elimination of some N atoms by the heat treatment. However, gaseous ammonia treatment increases the nitrogen content of the carbon spheres, where nitrogen content of 1.69 wt% is achieved for NPSRCSs. The advantage of the doping nitrogen method is that the specific surface area and pore volume of carbon materials have almost no apparent

deterioration, compared with impregnation method (Meng et al., 2019), which is in favor of keeping physical adsorption as well as strengthening chemical adsorption of CO₂.

The presence of nitrogen species on the carbon surfaces is further confirmed by XPS on the N1s signal. In Fig. 3, the curve fittings of the N1s spectra yield five main components with binding energies at 397.9, 399.2, 400.6, 401.7 and 402.8 eV, which can be assigned to pyridinic nitrogen, amide, pyrrolic nitrogen, quaternary nitrogen and nitrogen oxide, respectively (Zhang et al., 2016; Zhang et al., 2020; Raymundo-Piñero et al., 2003).

Fig. 4a shows TGA curves of PSRSs and OPSRSs, in which a gradual decrease in the weight loss curve can be clearly observed. TGA curve of PSRSs can be divided into three sections (Zhang et al., 2021), corresponding to the loss of adsorbed atmospheric gases (CO₂ and H₂O) at a temperature below 180 °C, the removal of terminal groups and further cross-linking/condensation reactions at a temperature range from 180 to 320 °C, the decomposition of bridged methylene into styrene-divinylbenzene at a temperature range from 320 to 600 °C and the further degradation of styrene to carbonaceous structure above 600 °C. After air pre-oxidization, a weight loss for OPSRSs at a temperature range from 180 to 320 °C disappears, being attributed to previous cross-linking of C-C skeleton at oxygen condition. In addition, the carbon retention of OPSRSs can reach 62.7% at 810 °C, higher 20.8% than that of PSRSs. Fig. 4b presents typical XRD patterns of PSRSs PSRCs and NPSRCs, respectively. Only a broad diffraction peak at about $2\theta = 17^\circ$ suggests that PSRSs belong to a kind of amorphous carbon. However, the broad diffraction peak shifts to high diffraction angle at about $2\theta = 23^\circ$, and the other peak at about 43° appears for as-prepared PSRCs and NPSRCs after high temperature treatment, they could be indexed as 002 and 10 diffraction peaks of turbostratic carbon. Consequently, PSRCs and NPSRCs prepared by this method have a turbostratic graphite structure.

Adsorption capacities of CO₂ on PSRSs, PSRCs and NPSRCs at 30 °C and 1 atm are shown in Fig. 5. Only a low adsorption capacity of 1.4 mmol g⁻¹ can be obtained, being attributed to less micropore volume, although PSRSs have a high specific surface area of 805.75 m² g⁻¹. As for PSRCs, the adsorption capacity is up to 2.82 mmol g⁻¹, which is 2 times higher than that of PSRSs. This is mainly due to the presence of abundant micropores resulting from steam activation, especially the pores ranged from 0.5 to 0.6 nm, indicating ultrafine micropores play an important role in adsorption of CO₂. Remarkably, by doping nitrogen-containing functional groups, NPSRCs exhibits a high CO₂ adsorption capacity of 3.2 mmol g⁻¹, despite decreased specific surface area and micropore volume (Table 1). The explanation is that radicals such as NH₂, NH and H resulting from ammonia decomposition at high temperature can react with carbon active sites to form functional groups, such as -NH₂-, -CN, pyridinic nitrogen, etc. These nitrogen-containing functional groups are lewis base active sites for binding acidic CO₂. In addition, we compare the CO₂ adsorption rates and adsorption capacities of these samples with that of commercial activated carbons (ACs, Table 1). At a time of 8 min, the adsorption capacity of these spheres can reach equilibrium, whereas that of ACs is almost saturated till a time of 25 min, being associated with the tortuous diffusion pathways within the porous structure. A low CO₂ adsorption

capacity of 2.1 mmol g^{-1} can be obtained for ACs, indicating micropores of the carbon material is not fully utilized during CO_2 adsorption.

In order to study the nature of the basic groups grafted on the surface of carbon spheres, the CO_2 temperature-programmed desorption (CO_2 -TPD) is conducted on a Micromeritics AutoChem 2920 instrument equipped with a TCD. About 100 mg of sample is placed into a U-shape quartz reactor and pretreated at 120°C under helium flow (30 ml min^{-1}) for 30 min. When the temperature is decreased to 40°C , CO_2 adsorption is performed by flowing CO_2 (10 ml min^{-1}) for 30 min. Afterwards, the desorption experiment is carried out by purging helium gas (50 ml min^{-1}) through the sorbent bed and ramping the temperature from 40 to 200°C at a rate of $10^\circ\text{C min}^{-1}$. Talking into account the production of large amount of CO_2 and other components, resulting from decomposition of PSRSs (polymer) at a temperature ranged from 180°C to 300°C , only the TPD profiles of PSRCSs and NPSRCSs are presented in the work, as shown in Fig.6. Only a desorption peak for PSRCSs can be observed at around 75°C , suggesting pure physical nature of CO_2 adsorption. This also indicates almost no nitrogen-containing functional groups exist on the carbon material. However, after doping nitrogen-containing functional groups, CO_2 desorption of NPSRCSs presents two well defined maxima, at 75 and 95°C . The low temperature CO_2 comes from the desorption of physically adsorbed CO_2 , while at high temperature it probably comes from the desorption of chemically adsorbed CO_2 (Wang et al., 2012). The low chemical desorption temperature also suggests that weak chemical interaction of CO_2 with nitrogen-containing functional groups.

Variation in the CO_2 adsorption capacities versus temperature for these spheres is shown in Fig. 7. In general, these as-prepared spheres display the usual curve corresponding to a fall-off of CO_2 adsorption capacities as temperature is increased. About 30-40% decrease of CO_2 adsorption capacities for these samples at 75°C compared with 30°C , being attributed to the physical nature of the adsorption process. Clearly, compared with PSRCSs, nitrogen-containing functional groups for NPSRCSs have a obvious contribution to improve the CO_2 adsorption capacity by 19% at 75°C , although a high adsorption capacity increase by 13.4% can be obtained at 30°C , suggesting a enhanced binding force between nitrogen-containing functional groups grafted by gaseous ammonia treatment and CO_2 at high temperature.

Usually, large amount of water is inevitable exhausted from flue gas, accompanying with CO_2 , while the presence of water will influence the adsorption capacities of CO_2 on solid sorbents. Fig. 8 presents the effect of water on the CO_2 adsorption capacity for PSRCSs. The pure H_2O adsorption capacity of PSRCSs is only 0.46 mmol g^{-1} in a nitrogen flow containing 4 vol% H_2O at 30°C and 1 atm, being characteristic of the hydrophobic materials. When PSRCSs are blown with the mixture gas flow containing 96 vol% CO_2 and 4 vol% H_2O at 30°C and 1 atm, the CO_2 adsorption capacity of PSRCSs is still up to 2.6 mmol g^{-1} , a high capacity retention of 92.2%, suggesting a slight effect of H_2O on CO_2 adsorption of PSRCSs, that is,

no obvious competitive adsorption of H₂O and CO₂ on PSRCSs. Because activated carbon materials rely on dynamic principle to separate gases, CO₂ with a fast adsorption rate can occupy the pores of carbon materials, prior to H₂O.

For potential practical applications, in addition to high CO₂ adsorption capacity and fast adsorption rates, a long-term cyclic stability and low regenerability temperature for solid sorbents are crucial to reduce the application cost. Fig. 9 shows multiple cycles of CO₂ adsorption at 30 °C and desorption at 120 °C for PSRSs, PSRCSs and NPSRCSs. After 10 cycles, almost no decrease of adsorption capacity for PSRCSs can be observed, exhibiting an excellent cyclic stability. Nevertheless, the CO₂ adsorption capacities of PSRSs and NPSRCSs have a low drop by about 1.2% after 10 cycles, being attributed to the chemical binding between nitrogen-containing functional groups and CO₂. In addition, a low temperature of 120 °C for these samples is almost enough to desorption completely, compared with other solid sorbents such as hydrotalcite-like compounds (Gil et al., 2018), and hydroxide (Siriwardane et al., 2007).

Conclusions

High yield and proportion of carbons spheres with high specific surface area of 1274.95 m² g⁻¹ and reasonable pore size distribution consisting of micropores, mesopores and macropores were successfully prepared by pre-oxidizing and activating polystyrene-based macroreticular resin spheres. The carbon spheres exhibited a high CO₂ adsorption capacity of 2.82 mmol g⁻¹, excellent cyclic stability and low hygroscopicity. Further, after doping nitrogen-containing functional groups, a CO₂ adsorption capacity of 3.2 mmol g⁻¹ can be obtained. The results indicated that as-prepared activated carbon spheres with high specific surface area, good porous texture parameters and reasonable nitrogen-containing functional groups were promising solid sorbents for CO₂ capture.

Declarations

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Ethical Approval

Not applicable.

Consent to Participate

Not applicable.

Consent to Publish

Not applicable.

Authors Contributions

Xiaoxia Ren is the first author of this work, and is responsible for doing experiments and writing manuscript. Changming Zhang is the corresponding author of this work, and is responsible for designing, guiding and managing this work. Lifang Kou is responsible for characterization of field emission scanning electron microscopy and N₂ adsorption/desorption. Rongxian Wang is responsible for CO₂ adsorption test. Yaqi Wang is responsible for characterization of X-ray power diffraction. Rui Li is responsible for characterization of element analyze and X-ray photoelectron spectroscopy. All authors read and approved the final manuscript.

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Competing Interests

The authors have no competing interests.

Availability of data and materials

All data and materials generated or analysed during this study are included in this published article. for CO₂ capture.

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Table

Table 1 Physical properties and chemical compositions of PSRSs, PSRCSs and NPSRCSs.

Samples	Physical properties				Chemical compositions			
	S_{BET} (m ²	V_{micro} (cm ³	V_{total} (cm ³	ρ_{Bulk} (g N	N	O	H	C
	g ⁻¹)	g ⁻¹)	g ⁻¹)	cm ⁻³)	(wt%)	(wt%)	(wt%)	(wt%)
PSRSs	805.75	0.22	0.67	0.40	1.93	11.65	5.51	80.91
PSRCSs	1274.95	0.47	1.09	0.42	0.66	5.6	0.84	92.9
NPSRCSs	1198.43	0.46	0.90	0.42	1.69	7.59	1.11	89.61
AC	1800	0.91	0.99	0.23	0.00	3.81	1.13	95.06

Figures

Figure 1

a and b) Photograph and particle diameter distribution of as-prepared PSRCSSs. c and d) SEM images of surface and cross section of PSRSs. e and f) SEM images of surface and cross section of PSRCSSs.

Figure 2

a) Nitrogen adsorption-desorption isotherms and b) DFT pore size distributions of PSRSs and PSRCSs.

Figure 3

N1s XPS spectra of NPSRCSs.

Figure 4

a) TGA curves of PSRSs and OPSRSs. b) XRD patterns of PSRSs PSRCs and NPSRCs

Figure 5

CO₂ adsorption isotherms of PSRSs, PSRCSs, NPSRCSs and ACs using pure CO₂ flow at 30 °C and 1 atm.

Figure 6

CO₂-TPD curves of PSRSs PSRCSs and NPSRCSs.

Figure 7

CO₂ adsorption capacities vs. temperature for PSRCSs using pure CO₂ flow at 1 atm.

Figure 8

Effect of H₂O on the CO₂ adsorption on PSRCSs at 30 °C and 1 atm.

Figure 9

Multiple cycles of CO₂ adsorption-desorption of PSRSs (a), PSRCSs (b) and NPSRCSs (c) using pure CO₂ flow at 30 °C and 1 atm.