Adsorption and Regeneration Study of Polyethylenimine-Impregnated Millimeter-Sized Mesoporous Carbon Spheres for Post-Combustion CO₂ Capture

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Abstract

The feasibility of polyethylenimine (PEI)-impregnated Millimeter-sized mesoporous carbon spheres (MCSs) for post-combustion CO₂ capture is systematically studied over a wide range of adsorption and regeneration conditions. MCSs with developed mesoporous structure and good electric conductivity are used as supports, while high-molecular-weight PEI ($M_n \sim 10000$) is screened to be the optimal amine due to its thermal stability. At the optimal polyethylene glycol (PEG) loading of 20 wt.%, the mass/volume-based adsorption capacity is efficiently improved by 25.7% and 109.5%, respectively. The optimized adsorbent exhibits high equilibrium adsorption capacity of 163.4 mg/g for 15% CO₂ at 75 °C under dry condition, and it could be further enhanced to 187.5 mg/g at the relative humidity of 60%. The presence of O₂, SO₂, NO and NO₂ would lead to the decreased adsorption capacity after consecutive adsorption-desorption cycles, due to the irreversible chemical reaction. Moisture could inhibit the negative effect of O₂ but deteriorate the detrimental effects of SO₂, NO and NO₂. Depending on the good sphericity, uniform particle size, excellent thermal/electrical conductivity and good mechanical properties of MCS, PEI-impregnated MCS adsorbents could be directly used in fixed bed system and be applicable for thermal swing adsorption (TSA), vacuum swing adsorption (VSA) and novel electric swing adsorption (ESA) processes. The adsorbents could maintain fairly stable cyclic performance during the rapid VSA process, making rapid VSA of great potential for technical-economical post-combustion CO₂ capture.

Keywords: post-combustion CO₂ capture, polyethylenimine, mesoporous carbon spheres, adsorption, regeneration strategies

1. Introduction

Carbon capture and storage (CCS) is considered as a promising countermeasure against the foreseen environmental challenges caused by the excessive CO₂ emission [1]. CCS with particular reference to post-combustion CO₂ capture shows the greatest potential in retrofitting traditional power plants [2]. Current chemical absorption processes are facing great challenges for the high energy and cost penalties [3]. Therefore, the alternative technology based on solid amine adsorbents (amines immobilized within porous supports) has attracted extensive attention. It overcomes the drawbacks of low CO₂/N₂ selectivity and water impairment for commonly used activated carbons [4], zeolites [5], covalent organic frameworks (COFs) [6], and metal-organic framework (MOFs) [7]. Furthermore, to be competitive with liquid solvents, solid amine adsorbents should offer thermal, chemical, and mechanical stabilities under extensive cycles except for the substantially greater capacities and selectivity for CO₂ [6].

Recently, a variety of solid amine adsorbents have been developed to take into account of the amine types, the supports structure, the immobilizing techniques, the adsorption and regeneration strategies, and the results are quite promising [8-11]. Various amines have been investigated for solid amine adsorbents including alkanolamines [12], alkylamine [13], aminopolymers [14-16] and aminosilanes [17] etc., and among these polyethylenimine (PEI) is most commonly used due to its high CO₂ uptake/release capacity and good stability at the temperature from 20 to 90 °C. The main guideline for porous substrates is well-developed structural properties, especially high pore volume and surface area [18]. The widely adopted supports include zeolites [19, 20], porous carbons [21-24], mesoporous silica [15, 16, 25-28], mesoporous alumina [29, 30], macroporous

resin [31] and MOFs [32] etc. Among various porous candidates, mesoporous silica and carbons are most widely investigated, mainly because of their large pore size and high pore volume. A tradeoff between high amine loading and the residual surface area should be considered, since higher amine loading is often accompanied by increasingly strong diffusion limitations [33]. It is worth mentioning that the geometry and particle size of the supports are also important for practical application with respect to the pressure drop, bed void fraction, and required regeneration methods [34]. Currently, most adsorbents for CO₂ capture reported in the literatures are employed in the form of micrometer-sized powder or irregular particles, which is not appropriate to be used directly in a fixed-bed system due to high dust and severe pressure drop. Therefore, the adsorbents should be shaped to a desired macroscopic structure with excellent mass transport mechanical properties and then operated stably for extended periods under flue gas conditions.

The viability of the adsorbents for post-combustion CO₂ capture largely depends on an effective and low energy-consumed regeneration. Depending on the structural and chemical properties of the adsorbents, the regeneration could be achieved via temperature, pressure (or vacuum), concentration swing adsorption or a hybrid thereof [35]. Currently, the dominate regeneration strategy for solid amine adsorbents is based on the temperature swing adsorption (TSA) [13-15, 17, 21], mainly due to the simplicity of operation by increasing temperature and no limitation on the microscopic morphologies of the adsorbents. The weakness of TSA is the long heating and cooling time caused by the thermal inertia [36]. A novel cost-effective regeneration strategy, electric swing adsorption (ESA), has been proposed, which is intrinsically a TSA process. The electric current is directly passed through the saturated adsorbents, and the “in-situ” heating by the Joule effect facilitates the release of CO₂ [37]. ESA process could

combine the merits of independent purge gas flow, fast heating and cooling rate and low energy consumption. However, it puts forward high demand on the adsorbents, such as good electrical conductivity and consistency of material. Consequently, only conductive carbon supports [38-40] are the potential candidates for ESA operation. Other alternative options are pressure/vacuum swing adsorption (PSA/VSA). The technical and economic difficulties for PSA mainly lie in the compression of the enormous flow in the flue gas [41]. VSA is more promising for CO₂ capture from large point sources. However, such information including desorption time, regeneration efficiency, multi-cycle stability of solid amine adsorbents under different regeneration strategies is still very limited in the literatures.

In this work, we developed a practical amine-impregnated solid adsorbent for highly effective post-combustion CO₂ capture. The key to our adsorbent relies on using the millimeter-sized mesoporous carbon spheres (MCSs) as the supports. The well-developed 3D interconnected structure of MCSs could accommodate high amine loading and improve the dispersion of PEI. The good sphericity, uniform particle size, excellent thermal/electrical conductivity and good mechanical properties make MCSs be used directly in fixed bed system and be applicable for TSA, VSA and even ESA processes. Moreover, to improve the lifetime of the adsorbent, high-molecular-weight PEI was successfully screened and CO₂-neutral polyethylene glycol (PEG) additive was employed. Special examinations were focused on the effects of H₂O, O₂, SO₂, NO, NO₂ in the flue gas on CO₂ dynamic adsorption capacity and multi-cycle stability during the consecutive adsorption-desorption cycles. Furthermore, the regeneration of the adsorbents were systematically investigated by TSA, VSA and ESA processes, which provided a useful comparison to build a proper regeneration strategy for CO₂ capture.

2. Experimental

2.1 Materials

PEI with average molecular weight (M_n) of 600, 1200 and 10000 g/mol and colloidal silica sol (LUDOX@HS-30 colloidal silica, 40 wt. %) used were purchased from Sigma-Aldrich Company. PEG ($M_w=6000$) and other chemicals were purchased from Titanchem Co. and used without further treatment.

2.2 Synthesis of the mesoporous carbon spheres (MCSs)

The MCSs were prepared in kilogram-scale *via* a suspension polymerization assistant sol-gel method using colloidal silica sol as hard template, according to our previous report [42]. In a typical synthesis, 0.8 kg of resorcinol and 1.2 kg of formalin (37 wt. % formaldehyde) were dissolved in 10 L deionized water followed by adding 7 kg of colloidal silica sol with stirring. The solution was then diluted to 20 L and stirred at 40 °C for 2 h. Then the mixture solution was poured into a 50 L glass reactor containing paraffin oil and the mixture was continuously stirred at 250 rpm for 30 min at 85 °C. The hybrid hydrogel spheres were aged at 85 °C for 3 days and then directly dried at 80 °C in an oven for 24 h. The hybrid xerogel spheres were further carbonized at 800°C for 3 h in a nitrogen atmosphere. The MCSs were obtained by immersing the carbonized spheres in 15 wt. % NaOH solution for 24 h and then washed with distilled water until the pH was neutral and dried at 100 °C.

2.3 Preparation of the adsorbents

The MCSs based solid amine adsorbents were prepared by a wet impregnation method [43]. In a typical preparation, the predetermined amounts of PEI (and PEG) were dissolved in 100 g of methanol at 40 °C, and then 20 g of the MCSs were added to the above solution. The mixture was continuously stirred at 100 rpm for 4 h and then dried at 40°C for 3 h to remove methanol under vacuum condition in a rotary vacuum evaporator. The as-prepared adsorbents were

denoted as MCS-x(a)-y, where x, y represents the weight percentage of PEI and PEG in the adsorbent (MCS+PEI+PEG), respectively, and a represents the M_n of PEI.

2.4 Characterization

The morphologies of the spheres were observed under scanning electron microscopy (SEM, JEOL 7100F). Pore structure of the samples were obtained from N_2 adsorption/desorption isotherms at 77 K with a Quadrasorb *SI* analyser. Before the measurements, the samples were degassed in vacuum at 353 K for 12 h. The specific surface areas (S_{BET}) and pore size distributions (PSDs) were calculated from the Brunauer-Emmett-Teller (BET) method and Barrett-Joyne-Halenda (BJH) model, respectively. The total pore volumes (V_{total}) were estimated from the amount adsorbed at the maximal relative pressure of 0.985. The thermal stability of the adsorbents was carried out with thermogravimetric analysis (Q600 TGA, TA Instruments, USA). The adsorbents were heated to 800 °C at a rate of 10 °C/min with the nitrogen flow rate of 100 mL/min.

2.5 CO₂ capture measurements

To screen the suitable PEI and optimize the adsorption performance of the adsorbents, CO₂ adsorption from pure CO₂ at atmosphere pressure under dry conditions was performed on the thermogravimetric analyzer. Pure CO₂ (99.99%) and purity N₂ (99.999%) were used for the adsorption and desorption runs, respectively. Typically, about 15 mg of adsorbent was placed in an alumina sample pan. After the adsorbent was heated to 110 °C in N₂ (100 mL/min) for 100 min to remove the moisture and CO₂ adsorbed from the air, the temperature was decreased to 75 °C. Then the feed gas was switched to CO₂ (100 mL/min) for 40 min for the adsorption study. The CO₂ capture capacity of the adsorbent was calculated from the weight gain of the adsorbent during the adsorption process.

CO₂ dynamic adsorption at specified temperature and atmospheric pressure was conducted in a fixed bed with inner diameter of 10 mm. In a typical adsorption process, about 3.5 g of the adsorbent was packed in the middle of the stainless steel column supported with filter screen. The dry or humid CO₂/N₂ gas mixture with different CO₂ concentrations at a flow rate of 50 mL/min was then introduced through the column until the adsorbent was saturated. The flow rate of the gas mixture was controlled by a mass flow controller. To control the relative humidity (RH) of the gas mixture, CO₂/N₂ mixture was divided to two passageways. One part of CO₂/N₂ mixture passed over a bubbler-type humidifier and then mixed with the dry gas. The RH of the gas mixture was thus controlled by tuning the ratio of the humid and dry stream, and monitored by a moisture detector. Breakthrough curves for CO₂ were obtained by analyzing the CO₂ concentration of the effluent gas using the online gas chromatograph (Shimadzu GC-2014C). The adsorption capacity of the adsorbent was calculated from the breakthrough profile.

2.6 Regeneration strategies for adsorbents

Three different regeneration strategies, TSA, VSA and ESA were applied to investigate the desorption performance of the adsorbents. Regeneration efficiency defined as the ratio of the adsorption capacity of the regenerated adsorbent to that of fresh one, is used to evaluate the regeneration performance of the adsorbent.

For TSA process, the adsorbent was rapidly heated up to a specified desorption temperature under a N₂ flow of 50 mL/min in the fixed bed, followed by holding at the desorption temperature for 160 min. The desorption profiles were gained by analyzing the effluent gas streams using the gas chromatogram at regular intervals.

For VSA process, when the adsorption process was ended, the gas was switched off and the vacuum pump was started. The vacuum pressure was immediately decreased to about 3 kPa and lasted for specified time. Then adsorption process was conducted.

Fig. 1. Schematic of the adsorption column for electric swing adsorption

For ESA process, the adsorption column was slightly modified to apply electricity on the adsorbents, as shown in Fig. 1. Two sheets of flat-plate electrical connection were located on both sides of the spherical adsorbents, which can provide a uniform electrical circuit through the MCS-based adsorbents. After adsorption process, 6 V voltage was applied under a N₂ flow of 50 mL/min. When the temperature rapidly reached to 100-110 °C, the voltage was decreased to 2.5 V to maintain the temperature. The desorption profiles were gained by analyzing the effluent gas streams using the gas chromatogram at regular intervals.

3. Results and discussion

3.1 Characterization of the MCSs and adsorbents

Fig. 2. Photograph of the MCSs (a), SEM images of the MCSs (b, c) and MCS-50(10000)-20 (d, e) with different magnification

The support MCSs were prepared *via* a suspension assisted sol-gel method using resorcinol-formaldehyde resin as carbon precursor and colloidal silica sol as hard template. Systematic studies have been done in our previous report about the porosity and particle size control of the MCSs [45]. In this work, a scale-up preparation was carried out to provide kilogram-scale MCSs as the supports for CO₂ capture. The obtained MCSs (Fig. 2a) have an average particle size of 0.5 mm and high mechanical strength of about 12 N. The typical morphology of MCS is shown in Fig. 2b, which possesses a good spherical shape and a smooth surface without cracks. It can be clearly seen from the high magnification SEM image (Fig. 2c) that MCSs possess distinct three-dimensional carbon skeleton with interconnected mesoporous and macroporous structure. The detailed porous structure of the MCSs was analyzed by N₂ adsorption/desorption at 77 K. As

shown in Fig. S1, the MCSs exhibit typical IV isotherm, suggesting the mesoporous structure. The detailed porosity parameters are summarized in Table 1. The pristine MCSs have a specific surface areas (S_{BET}) of 944 m²/g and total pore volumes (V_t) of 2.87 cm³/g and an average pore size of 16.6 nm. The unique spherical morphology and developed mesoporous structure make the MCSs very beneficial as the supports for practical applications.

The solid amine adsorbents were prepared *via* a wet impregnation method using the MCSs as supports. After loading the spherical adsorbents still maintain smooth external surface as shown in Fig. 2c. High-resolution SEM image (Fig. 2d) show that the amine-impregnated MCSs still possess admirable mesoporous porosity, similar to the pristine mesoporous network of MCSs. After loading 50 wt. % PEI and different amount of diffusion additive (PEG), the adsorbents still remain a certain amount of residual mesoporosity, which could provide a large gas/solid interface and allow fast ingress of CO₂ within the adsorbents.

Table 1. Structural parameters of the MCSs and the adsorbents.

Samples	S_{BET}^a (cm ² /g)	S_{mic}^b (cm ² /g)	V_t^c (cm ³ /g)	V_{mic}^d (cm ³ /g)	D_p^e (nm)
MCSs	944	205	2.87	0.09	16.6
MCS-50 (10000)	156	0	0.74	0	28.5
MCS-50 (10000)-5	106	0	0.54	0	28.2
MCS-50 (10000)-10	83	0	0.38	0	29.0
MCS-50 (10000)-15	55	0	0.26	0	28.2
MCS-50 (10000)-20	36	0	0.13	0	30.1

^a BET surface area. ^b Micropore surface area. ^c Total pore volume. ^d Micropore volume. ^e BJH desorption average pore diameter.

3.2 Optimization of the adsorbents

For a regenerable adsorbent, the stability and lifetime are generally more important than its adsorption capacity. PEI is the most well-studied polymer amine for solid amine adsorbent due to its high amine density, however, how to further improve the stability of PEI-based adsorbent is rarely reported. Here in this work, we focus on further improving the performance of PEI-based adsorbents from the following two points: using PEI with high molecular weight and adding CO₂-neutral diffusion additive.

Fig. 3. Thermal stability of the adsorbents evaluated by TGA (a) and the effect of PEI molecular weight on CO₂ cyclic adsorption capacity (b)

Three branched PEI with average molecular weight (M_n) of 600, 1200 and 10000 g/mol were selected to study their CO₂ adsorption performance. Before CO₂ adsorption measurement, the thermal stability of the MCSs impregnated with different M_n of PEI was evaluated using TGA

analysis. Fig. 3a shows the weight loss in percentage vs. temperature, measured by heating up the adsorbents in nitrogen flow. The temperature ($T_{1\%/min}$) at which the rate of weight loss reaches 1%/min is chosen as the thermal decomposition onset temperature for a qualitative assessment of the thermal stability of the adsorbents (Fig. 3a inset). Apparently, the PEI with M_n of 10000 exhibits much higher thermal decomposition onset temperature of 228 °C than 178 °C and 170 °C for M_n of 1200 and 600, respectively. This result suggests PEI with higher M_n have better thermal stability. Furthermore, the cyclic adsorption capacity of these adsorbents with PEI of different M_n are tested using TG in pure CO₂ flow at 75 °C as shown in Fig. 3b. As expected, the adsorbent MCS-50 (10000) exhibit highest capacity retention after 10 adsorption-desorption cycles. However, its initial adsorption capacity is lower than these of the adsorbents with PEI of lower M_n , as reported in previous literature [44]. This should be due to the lower fluidity and larger steric hindrance of PEI with higher M_n , leading to higher CO₂ inner diffusion resistance.

Fig. 4. Effect of PEG content on the mass-based/volume-based CO₂ adsorption capacity (a) and the cyclic adsorption capacity of MCS-50-20 (b)

From a view of long-term cycles, PEI ($M_n \sim 10000$) is the best candidate, but its adsorption kinetic should be improved. In our earlier work, CO₂-neutral diffusion additives were introduced into the PEI, which could break the bulk amines or their CO₂ adsorption product (ammonium carbamates) from a compact entity into a dual polymer composite, thus promoting the CO₂ diffusion kinetics [45]. Furthermore, PEG has been used as the third component to improve the CO₂ adsorption capacity of the solid amine adsorbents [45-47]. Herein, a thermally-stable linear PEG with M_n of 6000 was introduced into the adsorbents as the diffusion additive. The effect of PEG content on the mass-based/volume-based capacity of the adsorbents is presented in Fig. 4a. In a control experiment, the MCS impregnated with PEG was also evaluated which exhibited a negligible CO₂ adsorption capacity. The mass-based/volume-based CO₂ adsorption capacity increases gradually with PEG content and reaches the maximum at the PEG loading of 20 wt.% with a pronounced enhancement of 109.5% for volume-based CO₂ adsorption capacity. Further increasing the PEG amount to 25 wt.%, the CO₂ adsorption performance decreases. This should be ascribed to the excessive loading of PEI and PEG (total 75 wt.%), resulting in the loss of most of available channel for CO₂ transport in the adsorbents. The introduction of PEG could create extra CO₂ transfer pathways and the presence of hydroxyl group in PEG could promote the formation of carbamate type zwitterions, therefore, amine groups would adsorb more CO₂ molecular[45, 48]. Moreover, the multi-cycle stability of the adsorbents could be further improved by introducing PEG. After 10 cycles, the capacity retention of MCS-50-20 is significantly improved up to 97.0%, compared to 94.2% of the PEG-free adsorbent (Fig. 4b). These results indicate that PEG plays a role not only in increasing the diffusion kinetics and

adsorption capacity but also in improving the cyclic performance. PEG might serve as a flexible matrix to buffer the volume change during the CO₂ adsorption-desorption process, restraining the macro-phase separation of PEI during the long-term cycles [45].

3.3 CO₂ dynamic adsorption performance

After optimizing the capacity and cyclic performance, the adsorbent MCS-50-20 with 50 wt. % of PEI (10000) and 20 wt. % of PEG (6000) was systematically investigated using the stimulated flue gas for post-combustion CO₂ capture.

Effect of gas flow rate, adsorption temperature and CO₂ concentration on CO₂ adsorption capacity

The effects of gas flow rate, adsorption temperature and CO₂ concentration on the adsorption capacity were firstly evaluated in a fixed bed. Fig. S2 (a, b) shows the CO₂ breakthrough curves and calculated CO₂ adsorption capacity of MCS-50-20 at 75 °C. As the gas flow rate increases, the breakthrough time and the corresponding adsorption capacity decrease, which is related with the residence time of CO₂ in the adsorption zone. At higher gas flow rate, residence time of CO₂ in the adsorption zone is shorter, resulting in insufficient time for all CO₂ molecules to adsorb on the active sites of amine groups. This is especially more prominent when more surface sites are taken up as adsorption process and the CO₂ molecules are difficult to diffuse deeper into the pores of adsorbents.

The effect of adsorption temperature on CO₂ adsorption performance is shown in Fig. S2 (c, d). The adsorbent exhibits a highest adsorption capacity of 163.4 mg/g at 75 °C in a 15% CO₂/N₂ flow. This temperature-dependent result suggests a diffusion-limited process for solid amine adsorbents [44, 49]. At 75 °C, the adsorption capacity increases gradually with the increasing

CO₂ concentration, as shown in Fig. S2 (f). For 5% CO₂, the adsorption capacity is only 112.4 mg/g, and it increases to 199.1 mg/g for 50% CO₂. The amine usage at different CO₂ concentration is listed in Table S1. The adsorption isotherm shows a typical Langmuir type (Fig. S3), demonstrating a good performance of MCS-50-20 over the wide CO₂ concentration range. Thus, these findings provide an insight towards the importance of mass transfer in the CO₂ adsorption process.

Effect of moisture and oxygen on CO₂ adsorption capacity

The presence of moisture is unavoidable in the flue gas or other industrial gas, therefore the effect of water on CO₂ adsorption capacity should be clarified. As presented in Fig. 5a, a series of dynamic adsorption are performed with the RH ranging from 0-60%. The adsorption capacity increases gradually with the increasing RH, and the maximum adsorption capacity of 187.5 mg/g achieves at the RH of 60%. These results reveal a positive effect of RH on the adsorption process, in good agreement the bicarbonate formation mechanism in previous reports [50, 51]. In addition, the cyclic performance of the adsorbent under the presence of 60% RH can improve to 98.6% vs. 97% for dry condition (Fig. 5b). This is possible due to the moisture could inhibit the formation of urea linkages, which are considered as the major irreversible by-product of CO₂ reaction with amines [52, 53]. Compared to physical adsorption using activated carbons or zeolites, the water tolerance should be one of key advantages of solid amine adsorbents, which eliminates the need to strictly control the humid of flue gas prior to adsorption.

Fig. 5. Effect of moisture (a) and O₂ (b) on CO₂ adsorption capacity

The effect of oxygen, another important component, was investigated both under dry and humid condition. After exposing the adsorbents to dry O₂-containing gas mixture (15% CO₂, 5% O₂, 80% N₂), the adsorption capacity significantly decreases by 7% to 154.4 mg/g for the second run and it consistently decreases as cycle number increases, as depicted in Fig. 5b. This result may be due to an oxidative degradation both at adsorption and regeneration process. In case of adsorption process, some active sites are occupied by O₂, leading to irreversible loss of active sites. Furthermore, high desorption temperature (110 °C) aggravates the oxidation reaction of PEI with O₂. However, after introducing 60% RH, the cyclic stability of MCS-50-20 in the 5% O₂-containing gas improves significantly. Water may form a thin layer on the surface of the adsorbents, which could slow down the diffusion of oxygen into the interior PEI, inhibiting the

oxidation degradation of PEI. This oxidation behavior of PEI-based adsorbents supported on MCSs is qualitatively similar to previous work on silica-supported PEI adsorbents [54].

Effect of the SO₂, NO and NO₂ on CO₂ adsorption capacity

Fig. 6. Effect of SO₂, NO, NO₂ on cyclic adsorption capacity of MCS-50-20 under dry condition (a) and RH of 60% (b)

Flue gas contaminants such as SO₂, NO, NO₂ could also interact with PEI and reduce its capability for CO₂ adsorption. To evaluate the effect of these active gases on CO₂ adsorption capacity and lifetime of the adsorbents, consecutive adsorption/desorption experiments were conducted both in the dry and wet steams. The corresponding CO₂ adsorption capacity of the adsorbents before and after exposure to SO₂/NO/NO₂ is displayed in Fig. 6. When exposing to the steams containing 100 ppm SO₂, NO and NO₂, respectively, the adsorption capacity

decreases after 10 cycles in the order of $\text{NO} < \text{NO}_2 < \text{SO}_2$. This recession may be attributed to the high affinity of the adsorbent towards the acid gas, especially SO_2 , resulting in the irreversible effect on CO_2 adsorption capability.

While 60% RH is introduced to the flue gas, it can be found that more severe effect on the CO_2 adsorption are caused by SO_2 , NO and NO_2 . The adsorption capacity rapidly decreases to 73.8%, 78.6% and 85.5% after 10 runs in the humid $\text{SO}_2/\text{NO}/\text{NO}_2$ -containing steam, respectively. The negative effect of water vapor is probably due to the high solubility of SO_2 , NO and NO_2 in water, leading to the enhanced adsorption of SO_2 , NO and NO_2 on the adsorbents. It is worth mentioning that the actual concentration of SO_2 and NO_2 in the flue gas after flue gas desulfurization (FGD) and selective catalytic reduction (SCR) treatments is about 2 and 20 ppm [55], respectively, much lower than the concentration used in this study, which will be benefit for the relative long-term and stable cycles of the adsorbents.

3.4 Regeneration strategies

A qualified adsorbent for practical application should possess high adsorption capacity coupled with good regeneration performance. Owing to unique advantages of the millimeter-sized MCS support, such as high mechanical strength, no dust, good thermal stability and electric conductivity, the as-prepared adsorbents could adopt various regeneration operations, such as TSA, VSA and ESA.

TSA process

Fig. 7. Desorbed CO₂ mass as a function of regeneration time (a), regeneration efficiency (b) and breakthrough curves (insert) at different regeneration temperature

For TSA process, the adsorption is performed at 75 °C, and the desorption is operated at 75, 90, 100 and 110 °C with the purge N₂. The outlet gas was monitored by GC, thus we can depict the curves of the desorbed CO₂ mass as a function of regeneration time (Fig. 7(a)). In the case of regeneration at 75 °C, the desorption is operated at the same temperature as adsorption, which could be also considered as a concentration swing adsorption (CSA) process [56]. However, this process cannot fully desorb CO₂ in 160 min with only 75% efficiency for the second run. At higher temperatures the adsorbed CO₂ can be easily removed. By raising the desorption temperature to 110 °C, the desorption could finish in 50 min (include the temperature raising period of ca.10 min). The regeneration efficiency could maintain very well after 10 adsorption-desorption cycles as shown in Fig. 5. Therefore, TSA is reliable to regenerate the MCS-

supported adsorbents, however, detailed heat management including heating, regeneration and cooling should be considered to maximize the regeneration efficiency.

VSA process

Fig. 8. Regeneration efficiency towards different vacuuming time (a) and regeneration efficiency under rapid VSA cycles (b)

Pressure swing adsorption (PSA) is one of the most widely used industrial processes for gas separation by lowering the operating partial pressure to regenerate the adsorbents. For solid amine adsorbents, the adsorption capacity is largely determined by the amount of amine groups, and the adsorption capacities at low pressures are very high, followed by a slow adsorption process to saturated state [22]. Thus, lowering the desorption pressure could bring about a larger gain than increasing the adsorption pressure. Herein, for VSA process, the adsorbed CO₂ is recovered at subatmospheric pressure and 75 °C, identical to the adsorption temperature. Fig. 8a

shows the regeneration efficiency towards different vacuum time. It can be seen that a high efficiency of 78% can be achieved through a rapid vacuum of 15 min. Further increasing the vacuuming time, the efficiency gradually increase but still cannot be fully recovered even vacuuming for 90 min. To balance the regeneration efficiency and the vacuum time, here we choose vacuum time of 15 min for evaluating the feasibility of VSA cyclic process. As shown in Fig. 8b, although the regenerated adsorbent delivers a low adsorption capacity compared to the fresh one, it could maintain fairly stable cyclic performance with only 4.6% drop after 10 cycles. Regardless of the vacuuming-consumed mechanical energy, the rapid VSA process should be of great potential for post-combustion CO₂ capture. Since the rapid swing cycles would reduce the amount of adsorbents needed and the cost for separation in terms of the enormous gas flow in typical power plants [57].

ESA process

The heat in ESA is generated by employing the electric current through the conductive materials instead of using a hot gas. In order to determine the desorption condition, the voltage-temperature relationships of the support and adsorbent was firstly investigated. The temperature changes of the support alone as a function of the input voltage is shown in Fig. 9a. At an input voltage of 3 V, the temperature of MCSs rises to 135 °C in 10 min. Further increasing the input voltage to 4 V, a sharp increase of temperature could be seen in a short time of 5 min, demonstrating the excellent electricity conductivity of the support. After impregnation, the conductivity of the adsorbent should be deteriorated, thus the voltage-temperature relationship of the adsorbent is different from that of the support. As shown in Fig. 9b, the temperature of the adsorbent slowly rise to 65 °C in 15 min at an input voltage of 4 V, while a temperature of 140 °C can be rapidly achieved at an input voltage of 6 V within 6 min. After turn off the electric

current, the temperature of the adsorbent can quickly decrease to the ambient temperature without cooling medium, giving a cost-effective process for ESA process.

Fig. 9. Temperature changes of MCSs (a) and MCS-50-20 (b) as a function of the input voltage and the adsorption/desorption curve with ESA for MCS-50-20 (c)

According to the relationship of temperature and input voltage, we employed 6 V voltage to heat the adsorbent. When the temperature rapidly reached to 110 °C in 4 min, the voltage was then turned down to 2.5 V to maintain the temperature at a range of 100-110 °C. The desorption curve is presented in Fig. 9c. Owing to the rapid heat rate, most adsorbed CO₂ can be released in

30 min, with a regeneration efficiency of 80% for the second run. To the best of our knowledge, this is the first time to employ ESA on solid amine adsorbents, which may explore a new acceptable desorption technology for post-combustion CO₂ capture. Further efforts on optimizing the continuous ESA process and improving the ESA regeneration efficiency will be made in the future work.

4. Conclusion

In summary, solid amine adsorbents based on polyethylene-impregnated mesoporous carbon spheres were prepared for post-combustion CO₂ capture. The well-developed structural characteristic, macroscopic spherical morphology, excellent thermal/electrical conductivity as well as considerable mechanical properties make the MCSs a superior support. PEI with M_n of 10000 shows the highest thermal stability and the corresponding adsorbent has the best cyclic CO₂ adsorption capacity. The addition of PEG as diffusion additives could efficiently improve the mass/volume-based adsorption capacity by 25.7% and 109.5%, respectively. Moreover, the adsorbents show good CO₂ adsorption capacity at the gas flow rate of 50-200 mL/min, adsorption temperature of 25-90 °C and wide CO₂ concentration of 5-50%. O₂, SO₂, NO and NO₂ could interact with the amine groups irreversibly, decreasing the available CO₂ adsorption active sites and thus decreases adsorption capacity in repeated adsorption/desorption cycles. The presence of moisture could lead to enhanced CO₂ adsorption capacity and inhibit the negative effect of O₂ but deteriorate the detrimental effects of SO₂, NO and NO₂. Owing to the unique structural and physicochemical properties of the MCSs, the adsorbent could be directly used in fixed bed and be regenerated by the TSA, VSA and ESA process. The rapid VSA process should

be a technical-economical option for post-combustion CO₂ capture. Moreover, a novel ESA process has been explored as a cost-effective desorption technology for solid amine adsorbents.

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Graphical Abstract

Schematic of the mesoporous carbon spheres based solid amine adsorbents and adsorption column for electric swing adsorption