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Title: Development of Polyethylenimine (PEI)-impregnated mesoporous carbon spheres for low-concentration CO_2 capture

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Abstract: A novel low-concentration CO2 capture material (PEI/MCS) was developed by loading polyethylenimine (PEI) over mesoporous carbon spheres (MCS) with high porosity. The effects of pore structure, PEI loading, capture temperature, and promoters on CO2 capture of PEI/MCS were studied. The MCS with perfect spherical morphology was successfully synthesized by a hard-template assisted reverse emulsion method. The pore structure of MCS was adjusted by tuning the ratio of carbon to silica (Si/C) in the precursors. With increasing the Si/C from 0.8 to 1.1, the pore volume of MCS increased from 1.25 to 2.68 cm3/g. The optimal PEI loadings depending on the pore volume of MCS were 45, 62.5, and 65wt.% for MCS-0.8, MCS-1.1, and MCS-1.5, respectively. The highest CO2 capture capacity (3.22 mmol/g) was achieved on 62.5PEI/MCS-1.1 at CO2 partial pressure of 0.05 bar (5 vol%, a typical concentration of the tail gas from natural gas power plant and natural gas processing plant) and temperature of 75 oC, outperforming most of the solid amine sorbents reported at similar condition. However, the cycling stability of PEI/MCS is poor at the capture-regeneration temperature of 75 oC. The promoters Span 80 and 1,2-epoxybutane did not show remarkable effect on the cycling stability of PEI/MCS at 75 oC. Decreasing the capture-regeneration temperature can significantly improve the stability of PEI/MCS and there is almost no CO2 capacity loss (regeneration >99.5%) when the temperature decreased to 50 oC. As a result of high CO2 capacity and excellent regenerability and stability, PEI /MCS will be one of the ideal candidates for CO2 capture in the future.

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Submitted to Catalysis Today

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Dear Editor and Referees,

We would like to submit our manuscript "Development of Polyethylenimine (PEI)-impregnated mesoporous carbon spheres for low-concentration CO_2 capture" for your consideration for publication in ***Catalysis Today.*** We feel that our work is of great importance and suitable for publication in your Special Issue: Proceedings 12th NGCS for the following reasons:

The development of novel materials and new technologies for CO_2 capture and storage has received great attentions due to the global warming issues. Among different carbon capture and storage (CCS) technologies, post-combustion CO_2 capture is more promising, because this technology can be easily retrofitted into the existing power plants. There are two conventional options that the CO_2 can be captured in existing power plants: absorption by amine solvents and adsorption by solid sorbents. Amines absorption has been widely used in industry, but it has faced several challenges, such as low energy efficiency and high cost. In addition, the amine solvent loss due to regeneration as well as its degradation has resulted in challenges and environmental concerns. The CO_2 capture by solid materials may diminish the environmental impact of the CO_2 capture and at the same time result in a lower energy penalty, thus solid adsorption process may be an alternative to achieve CO_2 capture from existing power plants, especially natural gas power plant with low CO_2 concentration (3-5 vol%). Apart from CO_2 capture from power plant, CO_2 emission reduction is also very much needed from natural gas processing plant. Natural gas is a mixture of gases. It is typically at least 90 per cent methane, plus other hydrocarbons such as ethane and propane. Natural gas often also contains gases such as nitrogen, oxygen, carbon dioxide and sulphur compounds; and water. Gas containing small volumes of these impurities can still be used as fuel, but gas with high volumes cannot be burned efficiently and safely. An example is the natural gas produced at the Sleipner Field in the North Sea. This gas contains unusually high levels (about 9 per cent) of CO_2, but customers buying the gas want CO_2 levels less than 2.5 per cent. Generally, amine solvent is used to remove the CO_2, which is not energy efficient and environmentally friendly. Therefore, an urgent need is required to tackle this, thus solid sorbent is assumed to be a potential solution.

In this work, a novel low-concentration CO_2 capture material (PEI/MCS) was developed by loading polyethylenimine (PEI) over mesoporous carbon spheres (MCS) with high porosity. The effects of pore structure, PEI loading, capture temperature, and promoters on CO_2 capture of PEI/MCS were studied. The MCS with perfect spherical morphology was successfully synthesized by a hard-template assisted reverse emulsion method. The pore structure of MCS was adjusted by tuning the ratio of carbon to silica (Si/C) in the precursors. With increasing the Si/C from 0.8 to 1.1, the pore volume of MCS increased from 1.25 to 2.68 cm^3/g. The optimal PEI loadings depending on the pore volume of MCS were 45, 62.5, and 65wt.% for MCS-0.8, MCS-1.1, and MCS-1.5, respectively. The highest CO_2 capture capacity (3.22 mmol/g) was achieved on 62.5PEI/MCS-1.1 at CO_2 partial pressure of 0.05 bar (5 vol%, a typical concentration of the tail gas from natural gas power plant and natural gas processing plant) and temperature of 75 ^{o}C, outperforming most of the solid amine sorbents reported at similar condition. However, the cycling stability of PEI/MCS is poor at the capture-regeneration temperature of 75 ^{o}C. The promoters Span 80 and 1,2-epoxybutane did not show remarkable effect on the cycling stability of PEI/MCS at 75 ^{o}C. Decreasing the capture-regeneration temperature can significantly improve the stability of PEI/MCS and there is almost no CO_2 capacity loss (regeneration >99.5%) when the temperature decreased to 50 ^{o}C. As a result of high CO_2 capacity and excellent regenerability and stability, PEI /MCS will be one of the ideal candidates for CO_2 capture in the future. This paper is original, not under consideration for publication elsewhere, and all authors are aware of the submission and agree to its publication. We hope our paper is accepted for publication in ***Catalysis Today*** and we are looking forward to hearing from you soon.

Thank you for your time and concern.
Sincerely yours,
De Chen

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Dear Editor and Reviewers,

First of all, we truly appreciate all the constructive comments and suggestions from the reviewers, by which our article is improved a lot. Here we provide the changes and reply to the comments.

Reviewer #1:

1. The graphical abstract is too blurry. I'd suggest to improve the resolution.

Reply:

A new graphical abstract with high resolution was added in the revised manuscript.

2. It'd be better to compare the adsorption and regeneration performance between PEI/MCS (this study) and previously reported PEI-modified solid capture materials.

Reply:

We have compared the adsorption capacity and the literature value reported at similar condition (J. Am. Chem. Soc. 131 (2009) 5777, Chem. Eng. J. 361 (2019) 294, Microporous Mesoporous Mater. 62 (2003) 29, Energy Fuels 25 (2011) 456, Chem. Commun. 24 (2009) 3627, AIChE J. 61 (2015) 972) . The highest CO_2 capture capacity (3.22 mmol/g) was achieved in this work on 62.5PEI/MCS-1.1 at CO_2 partial pressure of 0.05 bar and temperature of 75 ^{o}C, outperforming most of the solid amine sorbents reported at similar condition (Page 14). The regeneration performance between PEI/MCS and previously reported PEI-modified solid capture materials was compared in the revised manuscript (Page 19).

Reviewer #2:

1. The quality of the graphical abstract needs to be improved. It cannot be read clearly (perhaps caused by the conversion of the file format).

Reply:

A new graphical abstract with high resolution was added in the revised manuscript.

2. The amount of PEI in MCS is not quantified after the synthesis.

Reply:

During the synthesis of PEI/MCS, almost all the PEI was impregnated into the pores of MCS. The surface of PEI/MCS (Fig. 2) and wall of the vial are very clean, and no PEI was lost during the synthesis. Therefore, the amount of PEI after the PEI/MCS synthesis equals the value y in yPEI/MCS-x (Section 2.1 Page 6).

3. What is the CO_2 adsorption capacity of MCS? It is useful to include the result of CO2 capture on MCS as a control experiment.

Reply:

The MCS-1.1 almost did not adsorb CO_2 at 75 ^{o}C in 5%CO_2 , the capacity is below 0.01 mmol/g (0.002 mmol/g, Fig. R1). Thus, it does not affect the CO_2 capture results of PEI/MCS. The CO_2 adsorption result of MCS was added in the revised manuscript (Page 17).

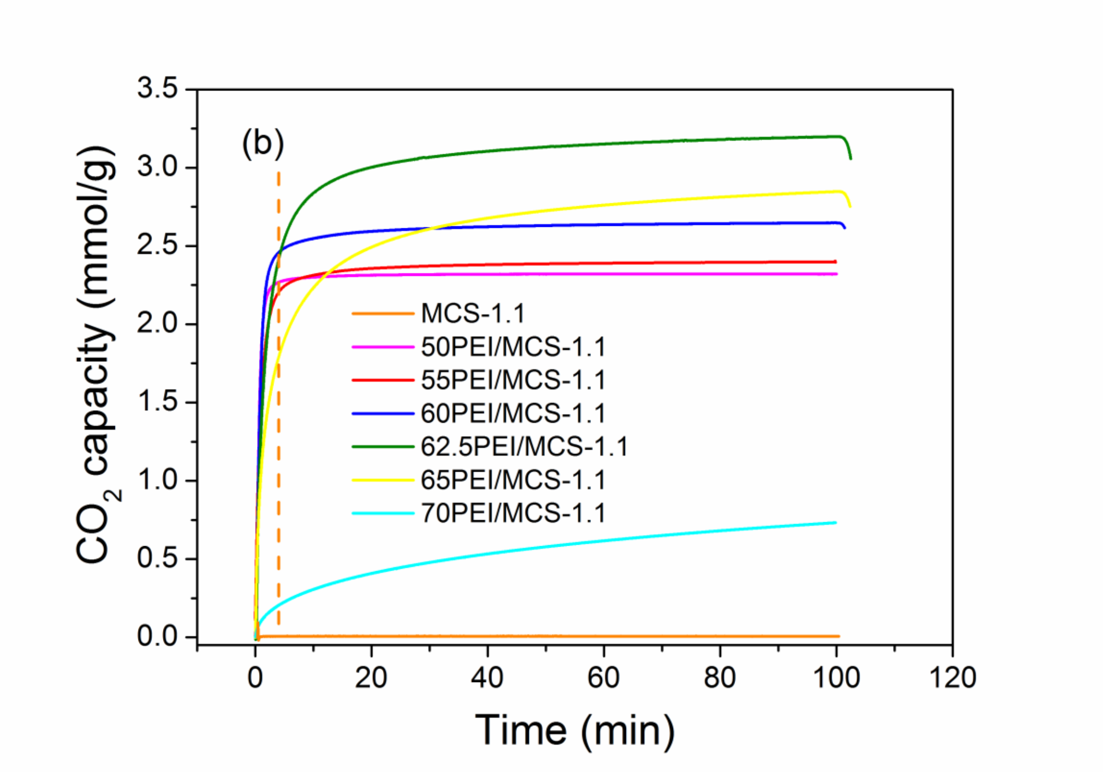

Fig. R1 CO_2 capacity of MCS and PEI/MCS

4. The authors reported a negative effect of the regeneration cycle at 75 ° C on CO_2 capacity. They attributed the negative effect to the trace K residual in the MCS. Please give a detailed explanation. It would be useful to support the claim with literature.

Reply:

According to our results (Fig. 9 in the revised manuscript) and the literature (Guo et al., Applied Energy, 129, 17-24), the poor regeneration performance at 75° C on CO_2 capacity could not be attribute to the negative of K. Guo et al. 's work indicated that K had a positive effect on the stability of PEI supported activated carbons. The decay of the CO_2 capacity at 75 ^{o}C might be caused by many factors, such as the loss of PEI due to the weak interaction with carbon surface, the oxidation of PEI by oxygen containing groups in MCS or by other unknown reasons. We have made revision on the reason of the deactivation in the revised manuscript (Page 19).

5. The authors proposed to use PEI/MCS for CO_2 *capture at low concentration. Their rationale is based on the fact that the tail gas from natural gas power plant contains a low partial pressure of* CO_2 *(approximately 0.05 bar or 5 vol%). In order to justify the case, it is better to comment on the potential application of PEI/MCS on a mixed gas stream containing* CO_2*. The results presented in this paper is on* CO_2 *only.*

Reply:

The capture of CO_2 on the PEI/MCS is based on the reaction between acidic CO_2 and basic amine group (-NH_x), and thus the capture of CO_2 is selective. Except for CO_2, there are also steam, O_2, SO_x, and NO_x in the tail gas of the gas power plant. The steam usually shows a positive role in the CO_2 capture on PEI impregnated porous materials. The small contents of O_2, SO_x, and NO_x might also have effect on the CO_2 capture at 50 ^oC. The effect of steam and other gases on the CO_2 capacity, cycling performance, and CO_2 capture mechanism will be studied systematically in next work. These comments were added on Page 21.

From:	Kumar R Rout <KumarRanjan.Rout@sintef.no>
Sent:	Thursday, August 29, 2019 9:11 PM
To:	Hongfei Ma; 陈庆军
Subject:	FW: Submit to the Special Issue of Catalysis Today - NGCS12

photo

Kumar Ranjan Rout
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From: "EEStangland@dow.com" <EEStangland@dow.com>
Reply to: "EEStangland@dow.com" <EEStangland@dow.com>
Date: Thursday, 29 August 2019 at 21:07
To: Kumar R Rout <KumarRanjan.Rout@sintef.no>
Subject: Submit to the Special Issue of Catalysis Today - NGCS12

Image removed by sender.

Dear Kumar Rout,

We are pleased to announce that the Catalysis Today portal to submit your conference proceedings article for the 12th Natural Gas Conversion Symposium in San Antonio is now open. After generating an author profile for Catalysis Today, you and your co-authors may now submit your paper by selecting the article type as *SI: Proceedings 12th NGCS*. The editorial team thanks you for your patience as we set up and communicated this portal.

As a reminder from our previous communication, this issue will have an open and peer reviewed submission process available to all oral presenters at the Symposium. While we cannot include all oral presentations from the conference, we have agreed to a format that will publish about 60 papers at about 5 printed pages apiece. We hope that this will generate sufficient interest to highlight in more detail the specific work you presented at the conference. If we have more than 60 submissions, we will use the peer review process to select the final included papers.

The timeline for the special issue will be as follows:

- First submission date: Open now
- Final submission date: October 15, 2019
- Deadline to complete all peer reviews: March 15, 2020
- Publication of Special Issue: May 15, 2020

Please let us know if you have any questions, and we look forward to your submission and the documentation of the exciting science from the 12th Natural Gas Conversion Symposium.

Best regards from your editors,

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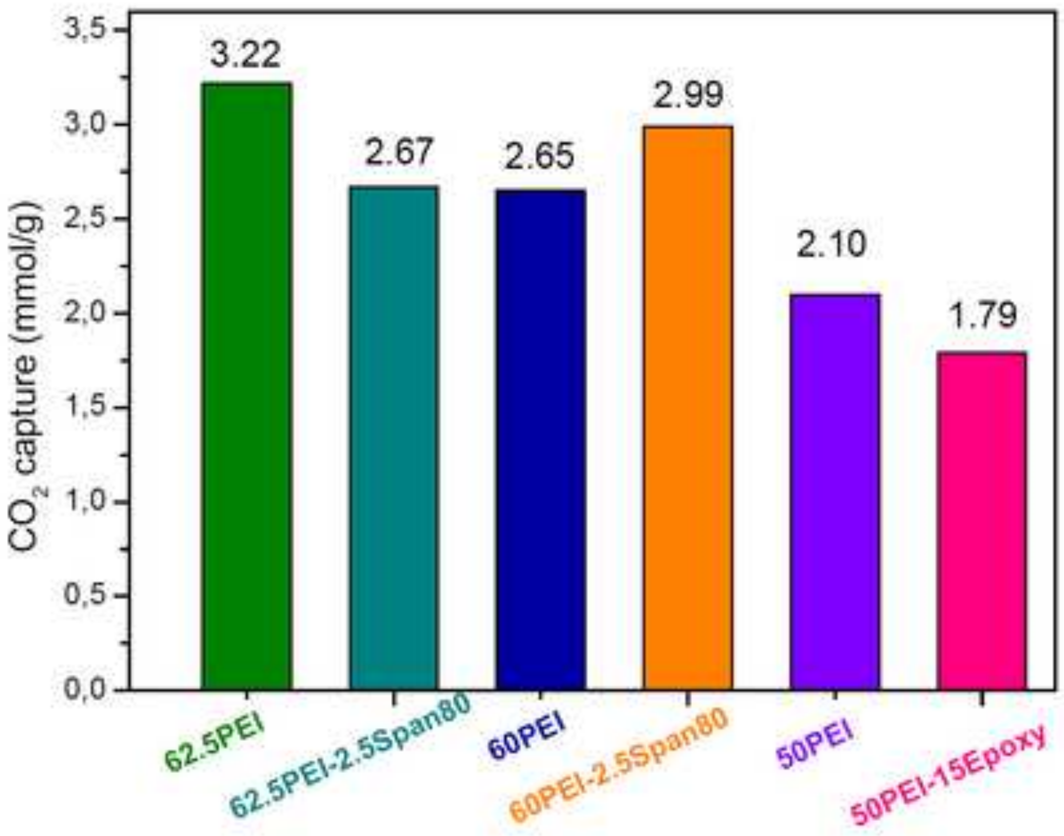
Highlights

- Polyethylenimine over mesoporous carbon spheres solid sorbent for CO_2 capture.
- CO_2 capture capacity (3.22 mmol/g) was achieved on 62.5PEI/MCS-1.1.
- PEI /MCS will be one of the ideal candidates for CO_2 capture in the future.

***Graphical Abstract (for review)**



Development of Polyethylenimine (PEI)-impregnated mesoporous carbon spheres for low-concentration CO_2 capture

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[1] Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), 7491 Trondheim, Norway.

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A novel low-concentration CO_2 capture material (PEI/MCS) was developed by loading polyethylenimine (PEI) over mesoporous carbon spheres (MCS) with high porosity. The effects of pore structure, PEI loading, capture temperature, and promoters on CO_2 capture of PEI/MCS were studied. The MCS with perfect spherical morphology was successfully synthesized by a hard-template assisted reverse emulsion method. The pore structure of MCS was adjusted by tuning the ratio of carbon to silica (Si/C) in the precursors. With increasing the Si/C from 0.8 to 1.1, the pore volume of MCS increased from 1.25 to 2.68 cm^3/g. The optimal PEI loadings depending on the pore volume of MCS were 45, 62.5, and 65wt.% for MCS-0.8, MCS-1.1, and MCS-1.5, respectively. The highest CO_2 capture capacity (3.22 mmol/g) was achieved on 62.5PEI/MCS-1.1 at CO_2 partial pressure of 0.05 bar (5 vol%, a typical concentration of the tail gas from natural gas power plant and natural gas processing plant) and temperature of 75 ^oC,

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outperforming most of the solid amine sorbents reported at similar condition. However, the cycling stability of PEI/MCS is poor at the capture-regeneration temperature of 75 ^{o}C. The promoters Span 80 and 1,2-epoxybutane did not show remarkable effect on the cycling stability of PEI/MCS at 75 ^{o}C. Decreasing the capture-regeneration temperature can significantly improve the stability of PEI/MCS and there is almost no CO_2 capacity loss (regeneration >99.5%) when the temperature decreased to 50 ^{o}C. As a result of high CO_2 capacity and excellent regenerability and stability, PEI /MCS will be one of the ideal candidates for CO_2 capture in the future.

1. Introduction

The development of novel materials and new technologies for CO_2 capture and storage has received great attentions due to the global warming issues [1,2]. Among different carbon capture and storage (CCS) technologies, post-combustion CO_2 capture is more promising, because this technology can be easily retrofitted into the existing power plants [3,4]. There are two conventional options that the CO_2 can be captured in existing power plants: absorption by amine solvents and adsorption by solid sorbents [5,6]. Amines absorption has been widely used in industry, but it has faced several challenges, such as low energy efficiency and high cost [7]. In addition, the amine solvent loss due to regeneration as well as its degradation has resulted in challenges and environmental concerns. The CO_2 capture by solid materials may diminish the environmental impact of the CO_2 capture and at the same time result in a lower energy penalty [8,9], thus solid adsorption process may be an alternative to achieve CO_2 capture from existing power plants, especially natural gas power plant with low CO_2 concentration (3-5 vol%). Apart from CO_2 capture from power plant, CO_2 emission reduction is also very much needed from natural gas processing plant. Natural gas is a mixture of gases. It is typically at least 90 per cent methane, plus other hydrocarbons such as ethane and propane. Natural gas often also contains gases such as nitrogen, oxygen, carbon dioxide and sulphur compounds, and water. Gas containing small volumes of these impurities can still be used as fuel, but gas with high volumes cannot be burned efficiently and safely. An example is the natural gas produced at the Sleipner Field in the North Sea. This gas contains unusually high levels (about 9 per cent) of CO_2, but customers buying the gas want CO_2 levels less than 2.5 per cent. Generally, amine solvent is used to remove the CO_2, which is not energy efficient and environmentally friendly. Therefore, an urgent need is required to tackle this, thus solid sorbent is assumed to be a potential solution.

Recently, amine-modified solid materials have been widely used for CO_2 capture, due to the advantages of high CO_2 capture capacity, high selectivity and low energy consumption [9-12]. Two different pathways have been explored to prepare solid amine capture materials: the impregnation approach [13,14], in which mesoporous/microporous materials are impregnated with amine-rich polymers (such as polyethylenimine), and the "amine-grafting" approach [15,16]. Compared with grafting method, the impregnation method possesses low cost, convenient preparation and a larger number of amine introduced, is more promising for using in industry.

For polyethylenimine (PEI)-modified solid capture materials (such as SBA-15, MCM-41, and porous carbon, etc.) [10,17,18], CO_2 was mainly captured by amine groups ($-NH_x$) in the sorbents, so the capture capacity was probably determined by the amount of amine loading and the utilization efficiency of these amine functional groups. The amount of PEI loading was mainly determined by the pore volume of the support, and the utilization efficiency of PEI was affected by the specific surface area and surface chemistry of the support, which determined the distribution of PEI on the pore walls. For traditional microporous and mesoporous materials, such as activated carbons [19], zeolites [20], ordered mesoporous silica/carbon [17,21], and hierarchical porous silica [22,23], the pore volumes are relative small, which restricts the amount of PEI loading and limits the CO_2 capture capacity. The capture materials having both high loading amount and well dispersion of PEI should perform better performance for CO_2 capture.

Mesoporous carbon spheres (MCS) is a new kind of porous material with perfect spherical morphology, large specific surface area and huge pore volume, exhibiting high potential as a support of high PEI loadings for CO_2 capture [24,25]. The MCS can be prepared by the hard template assisted reverse emulsion method and the pore structure can be easily adjusted by tuning the content of silica template. A high loading and dispersion of PEI can be achieved in the MCS with large pore volume and high surface area. In addition, the high mobility and dust-free property, as well as the low pressure drop and high attrition resistance of the MCS [26], will make it suitable for the usage in the circulating fluidized bed or moving reactor for CO_2 capture. Except for a high CO_2 capacity, the regeneration and cycling stability is also crucial for the CO_2 capture materials. Literature showed that the introduction of promoters (such as PEG, Span 80, 1,3-butadienediepoxide, epoxy, etc.) could effectively improve the stability of the solid amine capture materials [11,12,27,28]. Capture and regeneration temperature is also very important for the CO_2 capture capacity and stability. Therefore, promoter and temperature might also affect the performance of PEI modified MCS CO_2 capture materials.

In this work, MCS with control mesoporous structure were prepared and impregnated with PEI for CO_2 capture. The effects of pore structure, amount of PEI loading, capture temperature, and promoters on CO_2 capture were studied. The results showed that MCS with a medium pore volume (MCS-1.1) is the best support for PEI loading. The PEI/MCS (62.5PEI/MCS-1.1) exhibited the CO_2 capture capacity up to 3.22 mmol/g at CO_2 partial pressure of 0.05 bar and temperature of 75 ^{o}C, outperforming most of the solid amine sorbents reported at similar condition. However, the cycling stability is very poor at the capture-regeneration temperature of

75 ^{o}C. At a lower capture-regeneration temperature of 50 ^{o}C, a much better cycling stability can be achieved in PEI/MCS.

2. Experimental

2.1 Preparation of MCS

MCS was prepared by a hard-template assisted reverse emulsion method using formaldehyde and resorcinol as the carbon precursors and silica nanoparticles (LUDOX® SM-30) as the template [24,25]. Paraffin oil and sorbitan monooleate (Span 80) were used as the disperse phase (oil phase) and surfactant. Formaldehyde, resorcinol and silica nanoparticles were first mixed in deionized water under stirring. After pre-polymerization at 45 °C for 20 min, the solution was transferred to a glass reactor containing a mixture of paraffin oil and Span 80. The hybrid polymer spheres were formed after the stirring with a speed of 200 rpm at 85 °C for 60 min. The original carbon-silica carbon hybrid spheres were obtained by pyrolysis of polymer spheres at 700 ^{o}C with the rate of 3 ^{o}C/min for 3 h in nitrogen atmosphere. The silica template was removed by 3 M KOH solution leaching at 80 ^{o}C for one night. Then, the MCS was obtained by washing with deionized water until the pH value close to 7 and drying for one night at 100 ^{o}C. In order to tune the pore structure of the MCS, different C/Si weight ratio (0.8, 1.1, 1.5) was used in this work. The synthesized MCS was named as MCS-x, where x is the C/Si weight ratio.

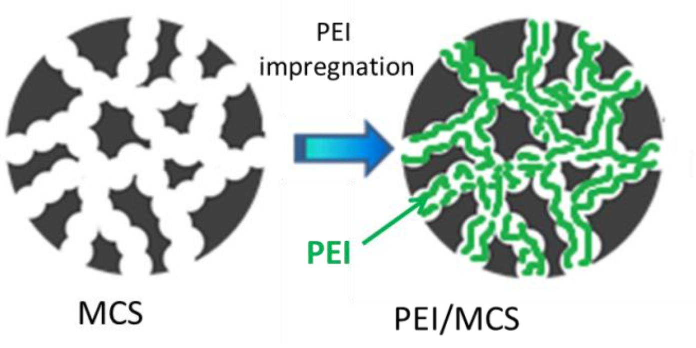

Fig. 1. Schemes of MCS and PEI/MCS

PEI impregnated MCS (PEI/MCS) were prepared by a wet impregnation method. In a typical preparation, the desired amounts of PEI (Mw of 600) were dissolved in 2 g of methanol at 35 ^{o}C under stirring for 30 min, and then 0.3 g of MCS was added to the above solution and further stirred for one night to remove methanol. The obtained capture material was denoted as yPEI/MCS-x, where y is the weight content of PEI (wt.%). Span 80 and 1,2-epoxybutane were used as promoters to improve the CO_2 capture performance. The Span 80 or Epoxy were first dissolved in methanol with PEI and then impregnate into MCS. Other preparation steps were same to those of PEI/MCS without promoters.

2.2 CO_2 capture test of PEI/MCS

CO_2 capture performance of PEI/MCS was measured by a thermogravimetric analyzer (TA Instrument Q600). The PEI/MCS (10~20 mg) was loaded into the sample chamber and pretreated at 100 ^{o}C under nitrogen (99.999%) for 100 min. The capture run was carried out using 5% CO_2 gas at the flow rate of 200 mL/min. The CO_2 adsorption isotherms were also tested by the same equipment at 75 ^{o}C. The regeneration of the spent PEI/MCS was carried out at different temperature in nitrogen for 100 min. Different temperatures were used for CO_2 capture and regeneration in this work.

2.3 Characterization

The N_2 adsorption-desorption isotherms of MCS and PEI/MCS were measured by a Micromeritics Tristar 3000 analyzer. The degassing of MCS was conducted at temperature of 200^{o}C for 12h. The degassing temperature of PEI/MCS was 60 ^{o}C and duration is 12h. The BET surface areas (S_{BET}) were analyzed by Brunauer-Emmett-Teller method. Micropore volumes (V_{mic}), micropore surface areas (S_{mic}) and external surface areas (S_{ext}) were obtained by t-plot method. Total pore volume was calculated by single point method at the relative pressure of

0.995. The pore size distributions were calculated from the analysis of the desorption branch of the isotherms using Barrett-Johner-Halendar (BJH) method. The morphologies of samples were observed under scanning electron microscopy (STEM, Hitachi S-5500) and digital camera.

3. Results and Discussion

3.1 SEM and TEM images of MCS and PEI/MCS

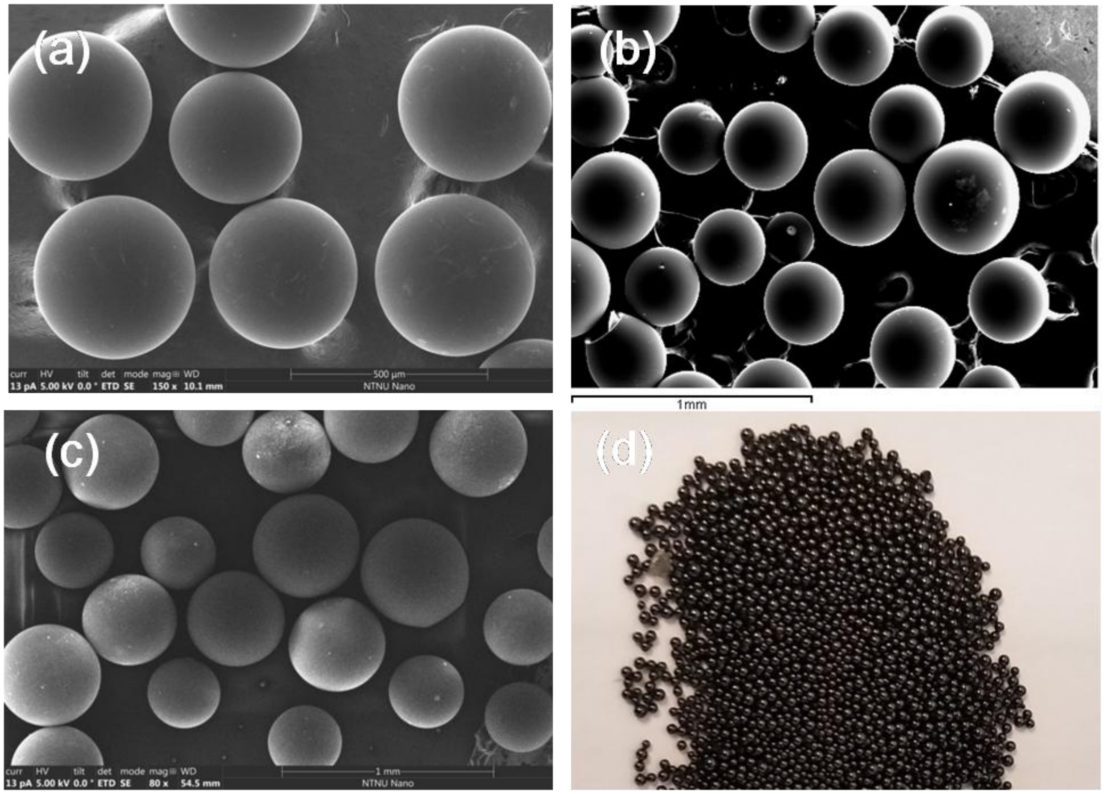

Fig. 2. SEM (a, b, c) of the MCS (a: MCS-0.8; b,d,MCS-1.1, c: MCS-1.5) and digital images (d, 5× magnification)

MCS were synthesized by a hard template assisted reverse emulsion method, and the pore structures were adjusted by the ratio of silica template to C precursor (Si/C ratio). The SEM and digital images of MCS with different Si/C ratio are shown in Fig. 2. The MCS exhibited excellent spherical morphology with clean and smooth external surface. The diameters of the MCS are very homogeneous and in the region of 0.3-0.4 mm. The Si/C ratio did not have obvious effect on the morphology and diameter of the MCS. The digital image of MCS-1.1 in Fig. 2(d) shows the excellent and homogeneous spherical structures, which possesses wonderful mobility and dust-free property. In addition, the advantages of low pressure drop and high attrition resistance of the spheres [26,29,30], will make MCS suitable for the usage in the circulating fluidized bed or moving bed reactor for CO_2 capture .

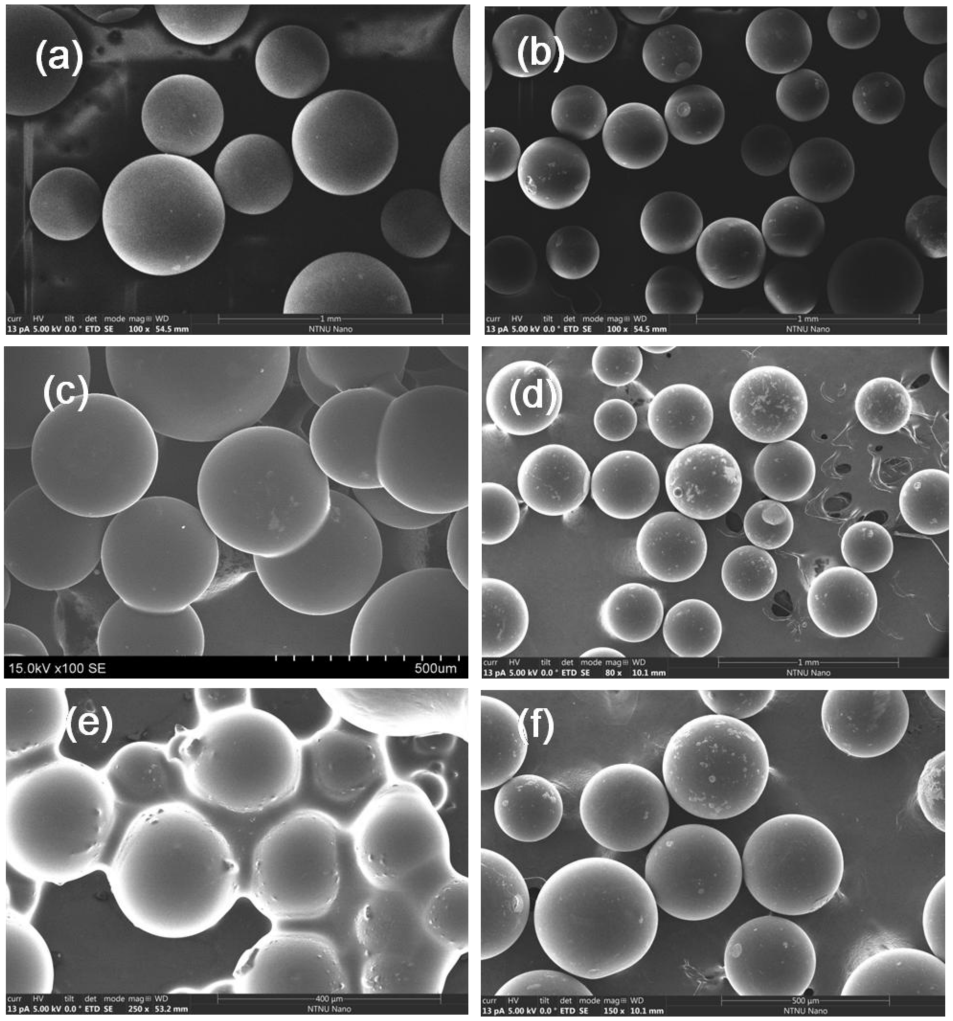

Fig. 3. SEM images the PEI impregnated MCS before and after CO_2 capture (a: 50PEI/MCS-1.1; b: 60PEI/MCS-1.1; c: 62.5PEI/MCS-1.1; d: 65PEI/MCS-1.1; e: 70PEI/MCS-1.1; f: 62.5PEI/MCS-1.1 after CO_2 capture)

The SEM images the PEI impregnated MCS before and after CO$_2$ capture are presented in Fig. 3. When the PEI loading is lower than 62.5% (Fig. 3 a, b, c) in MCS-1.1, the CO$_2$ capture materials maintained the clean and spherical morphology. This result indicated that most of PEI was located inside the pores of MCS-1.1 at the relative low PEI loading ($\leqslant$ 62.5wt%). When the PEI loading reached 65 wt%, some PEI particles can be found on the external surface of the spheres. Further increasing the PEI loading to 70%, all the pore of MCS-1.1 was saturated with PEI and the spheres were covered by PEI (Fig. 3e). After the CO$_2$ capture at 75 ^{o}C, the shape of the spheres was kept and small amount of PEI was found on the external surface of the spheres (Fig. 3f). This result indicated that some PEI went out from the pores of spheres during the high temperature degassing (110 ^{o}C) or CO$_2$ capture (75 ^{o}C).

3.2 Pore structure of MCS and PEI/MCS

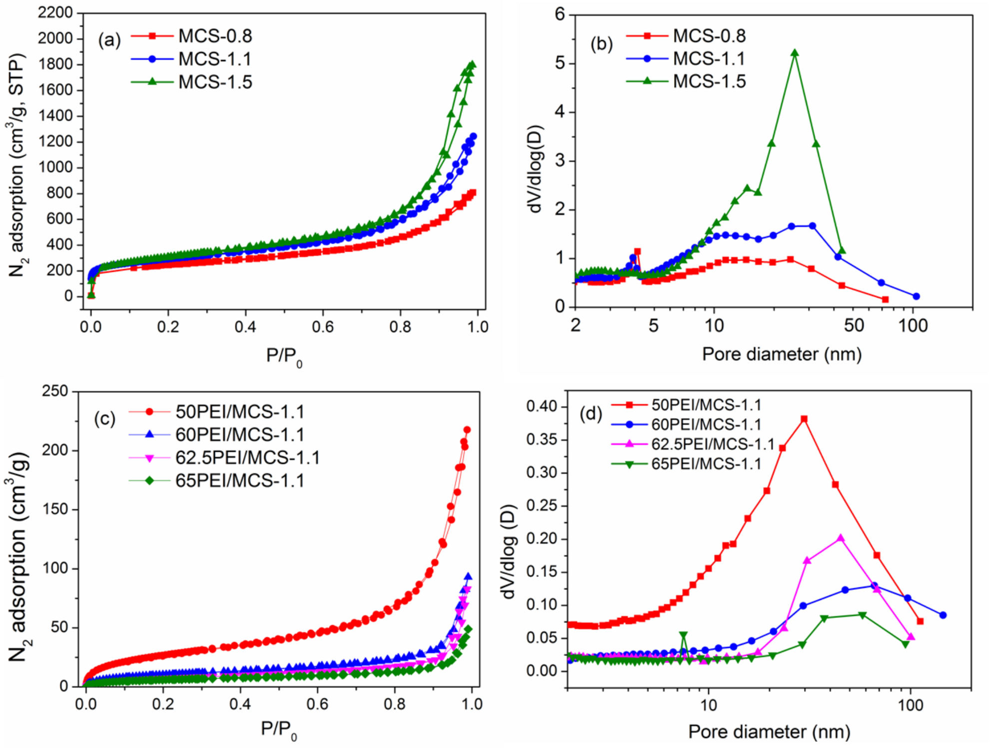

Fig. 4. Isotherms of the MCS and PEI/MCS with different pore structure

The N_2 adsorption-desorption isotherms and resultant pore size distributions of pristine and PEI impregnated MCS are shown in Fig.4. The pore structure parameters of these materials are summarized in Table 1. The N_2 adsorption-desorption isotherms of MCS with different Si/C ratio (Fig. 4a) belonged to the combination of Type I and IV isotherms according to the classification of IUPAC [31]. This result indicated the co-existence of micropores and the mesopores/macropores in the MCS. The micropore volumes (0.16-0.17 cm^3/g) of MCS are similar, but the mesopore/macroporous volume increased with the Si/C ratio (Table 1). It is inferred that the Si/C ratio mainly affected the mesopore/macroporous structure of MCS. The total volumes of MCS increased with the Si/C ratio and the maximum value was up to 2.68 cm^3/g when Si/C is 1.5. The specific surface areas of the MCS increased slightly from 817 to 1097 m^2/g with increasing the Si/C ratio. The pore size distributions of MCS are shown in Fig.4b. The pore size of MCS are mainly in the region of 2 to 100 nm, especially between 5 and 50 nm. With the increase of Si/C ratio, the pores with size between 5 and 50 nm increased. The average pore size of MCS also increased with the Si/C ratio (Table 1). The developed pore structure and large pore size of MCS allows a high amount of PEI loading with good dispersion.

After PEI loading, the N_2 adsorption capacities of the MCS decreased significantly (Fig. 4c). The BET surface areas and pore volumes decreased as the amount of PEI loading increased (Table 1). All the micropore surface area and pore volume disappeared after the introduction of PEI. Thus, the residual mesopores or macropores could play important roles for the CO_2 diffusion. When the PEI loadings are 62.5 wt% and 65 wt%, the specific surface areas are 28 and 22 m^2/g, respectively. This meant there were still some pores left even when the PEI loading were up to 62.5 wt% and 65 wt%. It is noted that there is no pore detected in 70PEI/MCS-1.1. All the pore of MCS-1.1 were blocked by the extremely high PEI loading of 70 wt%, corresponding to the SEM results (Fig. 3e).

Table 1. Porosity Parameters of MCS and PEI/MCS

Sample	S_{BET}[a] m^2/g	S_{ext}[b] m^2/g	S_{mic}[c] m^2/g	V_t[d] cm^3/g	V_{mic}[e] cm^3/g	D[f] Nm
MCS-0.8	817	523	294	1.25	0.16	7.6
MCS-1.1	1002	670	332	1.85	0.17	9.3
MCS-1.5	1097	868	229	2.68	0.17	10.8
50PEI/MCS-1.1	102	102	0	0.34	0	12.3
60PEI/MCS-1.1	40	40	0	0.14	0	14.3
62.5PEI/MCS-1.1	28	28	0	0.12	0	17.5
65PEI/MCS-1.1	22	22	0	0.08	0	13.8
70PEI/MCS-1.1	-	-	-	-	-	-

Note: [a] BET specific surface area, [b] External surface areas, [c] T-plot microporous surface areas, [d] Total pore volume calculated at relative pressure of 0.995, [e] T-plot microporous volume, [f] average pore diameter.

3.3 CO_2 capture performance of PEI/MCS

3.3.1 Effect of pore structure on the performance of PEI/MCS

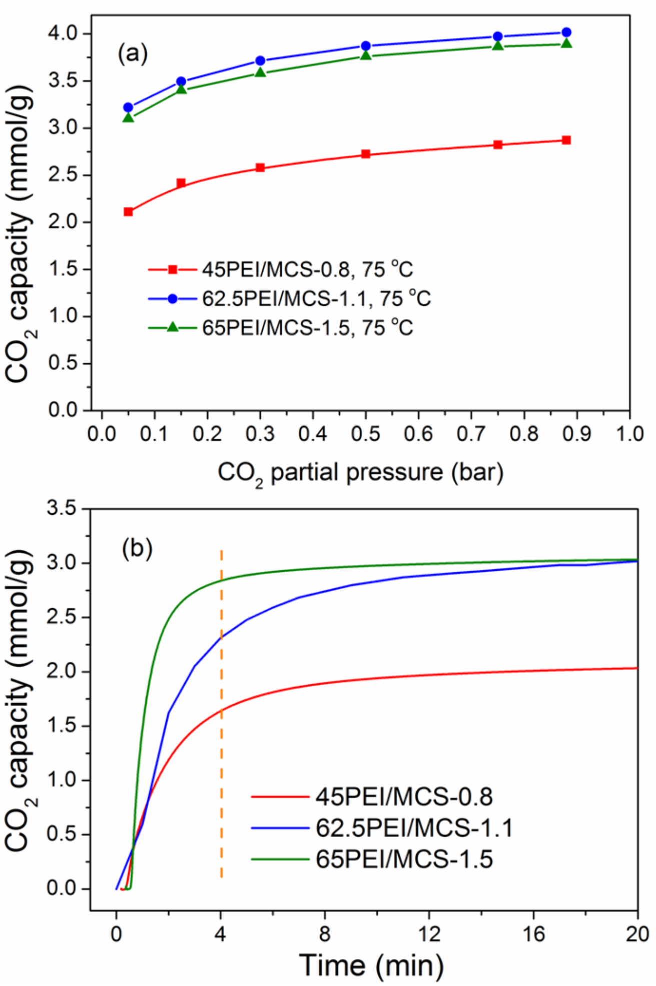

Fig. 5 CO_2 capture performance of PEI/MCS with different pore structure: a, isotherms (75 ^{o}C); b, adsorption kinetics (75 ^{o}C, 0.05 bar)

CO_2 capture capacities of PEI/MCS with different pore structure were tested by TGA at 75 ^{o}C, which is the optimal capture temperature for solid amine sorbents proposed by many researchers [10,11,32]. In this work, the optimal PEI loadings depending on the pore structure of

MCS were 45, 62.5, and 65 wt.% for MCS-0.8, MCS-1.1, and MCS-1.5, respectively. The effect of PEI loading on CO_2 capture will be discussed later using MCS-1.1 as an example. The isotherms of PEI/MCS with different pore structure are shown in Fig. 5a. The PEI/MCS exhibited high CO_2 capture capacity at low CO_2 concentration (0.05bar), which is more than 70% of that at 0.9 bar. The 45PEI/MCS-0.8 showed a much lower CO_2 capacity, comparing with 62.5PEI/MCS-1.1 and 65PEI/MCS-1.5. This is attributed to the lower PEI loading (45wt%) and smaller amount of site for CO_2 capture. For 62.5PEI/MCS-1.1 and 65PEI/MCS-1.5, similar CO_2 adsorption isotherms were achieved. Although with a lower PEI loading, 62.5PEI/MCS-1.1 exhibited a slightly higher CO_2 capacity than 65PEI/MCS-1.5. The MCS with medium pore volume and slightly lower PEI loading possessed the highest CO_2 capacity. This result suggested that pore volume and PEI loading are not the only factors determining the CO_2 capture capacity. The exposed PEI surface area and thickness of the PEI film are also crucial to the CO_2 capture capacity. The CO_2 capacity of PEI/MCS-1.1 was up to 3.22 mmol/g at CO_2 partial pressure of 0.05 bar and 75 ^{o}C, which is higher than most of PEI-based capture materials at similar condition [10,13,17,19-21,32,33]. As a result of the excellent CO_2 capture capacity at low partial pressure, PEI/MCS is promising for the application in low-concentration CO_2 removal from Nature gas power plant.

The capture kinetic curves of PEI/MCS are presented in Fig. 5b. The CO_2 capture rate in the first 4 minutes increased in the order of 45PEI/MCS-0.8 < 62.5PEI/MCS-1.1 < 65PEI/MCS-1.5. This result suggest that the material with a large pore size have a high capture kinetic. The large mesopores are benefit for the CO_2 diffusion and capture.

3.3.2 Effect of capture temperature

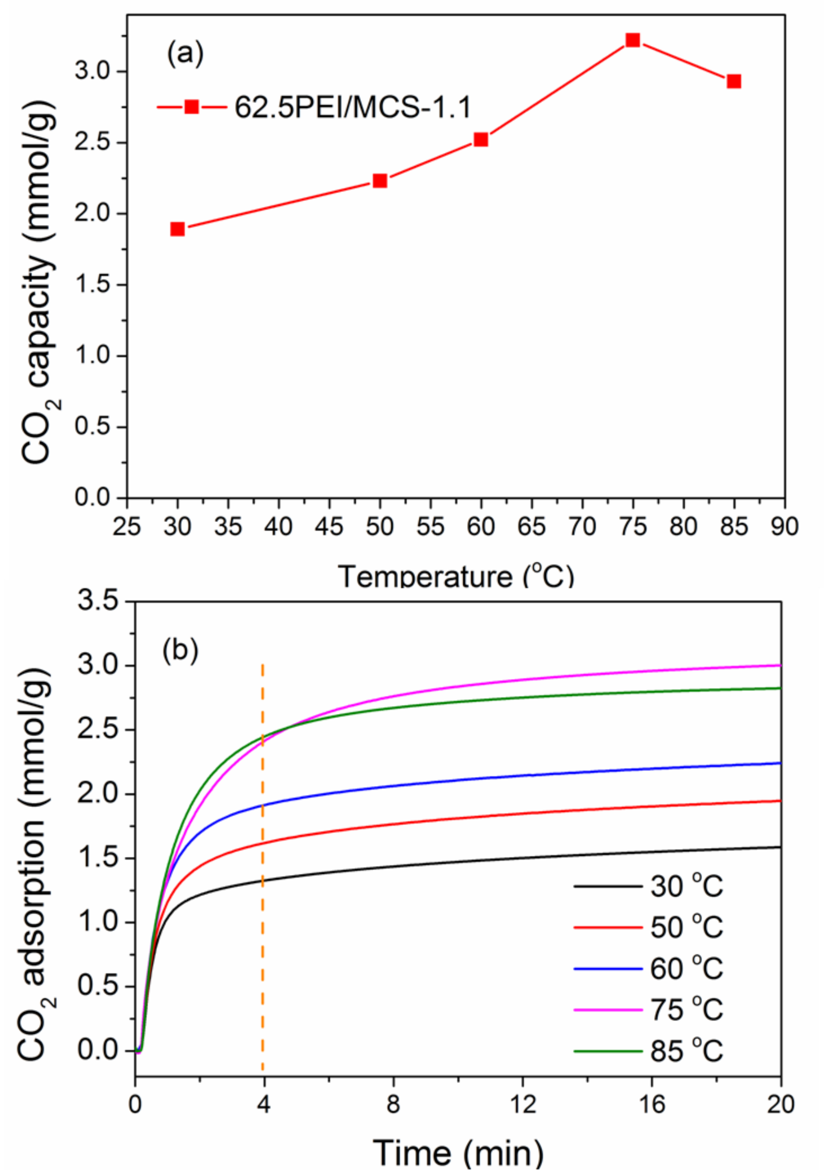

Fig. 6. Effect of temperature on CO$_2$ capture capacity (a) and kinetics (b) of 62.5PEI/MCS-1.1 (CO$_2$ partial pressure of 0.05 bar)

Temperature is one of the most important factors affecting the CO_2 capture capacity. The effect of temperature on CO_2 capture capacity and kinetics of 62.5PEI/MCS-1.1 is shown in Fig. 6. It can be seen that with the increase of temperature, the capture capacity first increased and then decreased. The optimal temperature is 75 ^{o}C for 62.5PEI/MCS-1.1, which is in agreement with the other PEI modified solid materials [10,11,32]. From the kinetic curves (Fig. 6b), the capture rate increased with the temperature in the first 4 minutes. This result indicated that capture kinetics are enhanced at higher temperature. The capture of CO_2 over PEI/MCS can be divided into three steps: the diffusion of CO_2 to the PEI surface from the gas phase, the diffusion of CO_2 from the PEI surface into the bulk of PEI films (internal diffusion) and the reaction balance between CO_2 and amine groups in the PEI molecules.[13]At the same space velocity, the concentration of CO_2 at the surface of the PEI is more or less the same at different temperature. And it is favorable for the reaction between CO_2 and PEI at low temperature due to the exothermic reaction. However, the low CO_2 capacity at low temperature is mainly due to the small CO_2 diffusion rate in the PEI films and most of the PEI was not utilized. With increasing the capture temperature, the diffusion of CO_2 is improved and the utilization efficiency of PEI is enhanced, which increase the capture capacities. However, at a higher temperature, the capture capacity was limited by reaction thermodynamic and decreased with further increasing the temperature. Therefore, the capture of CO_2 is both determined by the diffusion kinetics and the reaction thermodynamic. It can also be seen that the capture capacities of 62.5PEI/MCS-1.1 is larger than 2.23 mg CO_2/g at the temperatures from 50 to 85 ^{o}C. This result indicated that the PEI/MCS can be used in a wide temperature region.

3.3.3 Effect of PEI loading

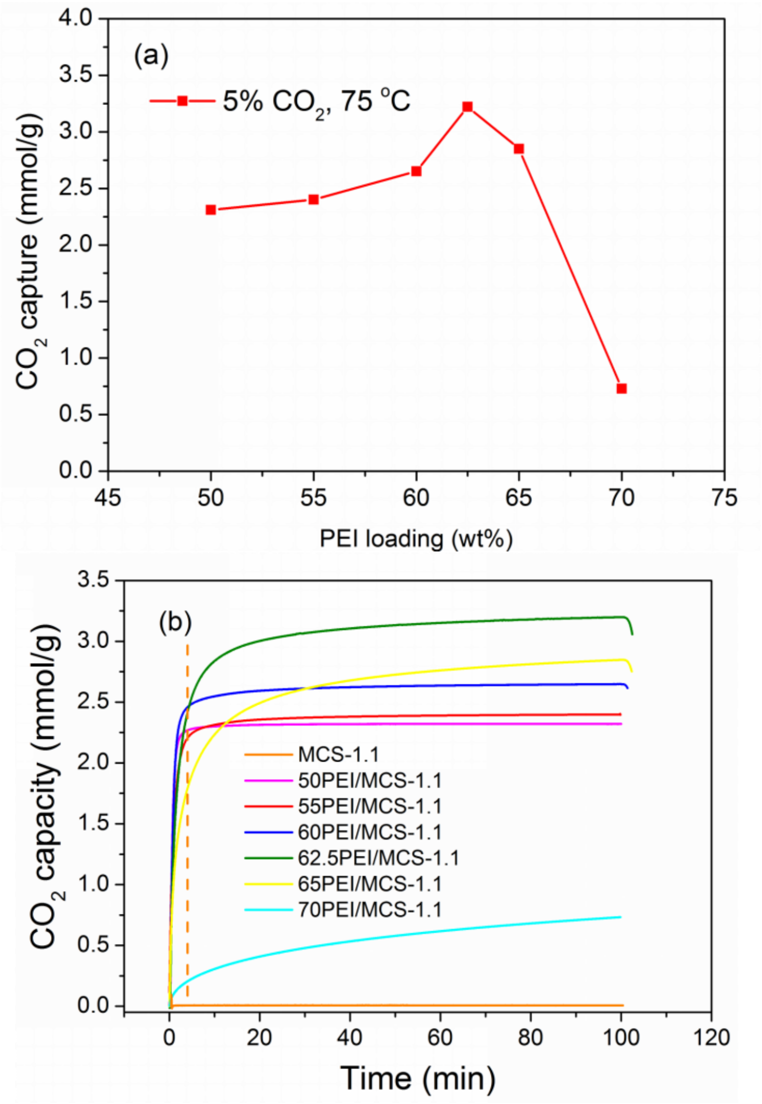

Fig. 7 **Effect of PEI loading on CO_2 capture capacity (a) and kinetics (b) of PEI/MCS**

Figure 7 shows the CO_2 capture curves of the PEI/MCS with different PEI loadings. The CO_2 capture capacities increased with the increase of PEI loading, achieved the maximums at the PEI loading of 62.5 wt.%, and then decreased. The MCS-1.1 without PEI loading had a negligible CO_2 capture capacity (below 0.01 mmol/g), and thus the support MCS almost did not adsorb CO_2. The capture of CO_2 over PEI impregnated porous materials was mainly determined by the reaction between CO_2 and amine groups in the PEI. So the capture capacity increased with the increase of PEI loading. However, excessive loading of PEI (>65 wt.%) could block the pores of the carbon support, resulting a low utilization of PEI. From the kinetic curves (Fig. 7b), the CO_2 capture rates are much lower when the PEI loading are higher than 65 wt.%. This is because the diffusion of CO_2 from the external surface into the internal PEI stored in the mesopores is very difficult, and most of the PEI was not utilized for capture CO_2.

3.3.4 Effect of promoters

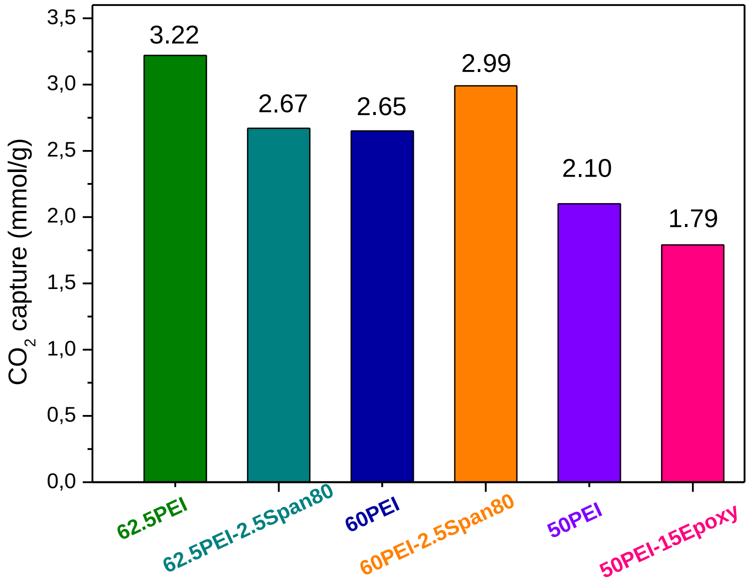

Fig. 8 Effect of promoters on CO_2 capture of PEI/MCS

As discussed above, the diffusion of CO_2 in the PEI film is a very important process to impact the CO_2 capture capacity. Literature reported that the introduction of promoters (such as span 80 and 1,2-epoxybutane) could improve the CO_2 diffusion, capacity or stability of the material [11,12,27,28]. In this work, we studied the effect of epoxy and span 80 on CO_2 capture of PEI/MCS, and the results are shown in Fig. 8. At the optimal PEI loading of 62.5wt%, the adding of surfactant Span 80 (2.5 wt%) had a negative effect on the CO_2 capacity. This is attributed to the pore block at the high total loading of PEI and Span 80 (65 wt%). At a lower PEI loading of 60 wt%, the introduction of 2.5 wt% Span 80 enhanced the CO_2 capacity, which is in agreement with the literature [11]. The promoter 1,2-epoxybutane (epoxy) also decreased the CO_2 capacity of PEI/MCS,as seen from Fig. 8. The effect of promoters on the stability of the capture material will be discussed below.

3.4 Regeneration performance

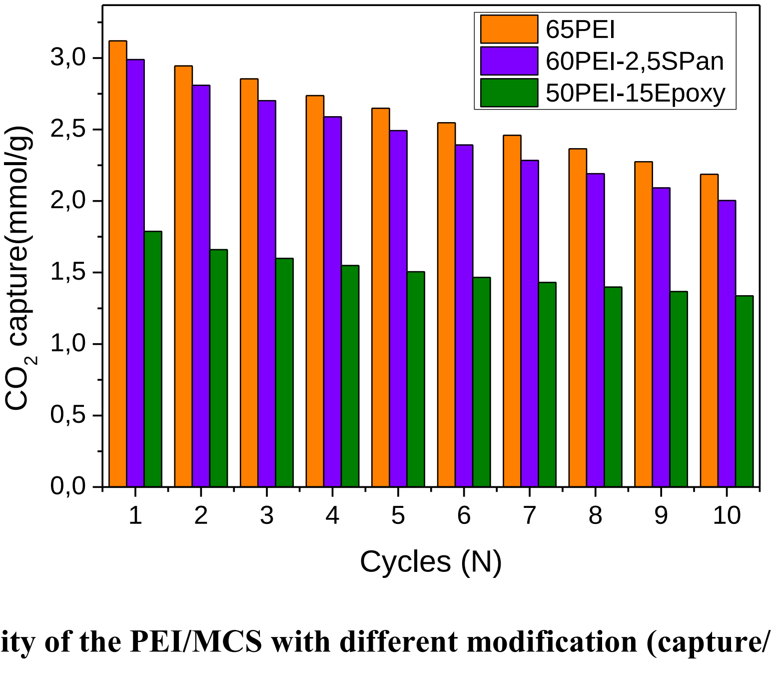

Fig. 9 Stability of the PEI/MCS with different modification (capture/regeneration temperature of 75 °C, CO_2 capture pressure of 0.05bar)

For practical application, the capture material should not only possess a high CO_2 capacity but also have excellent regenerability and stability in the capture-regeneration cycles. The regeneration of the spent capture material can be easily performed at same temperature (75 ^{o}C) using N_2 as a purge gas. Fig. 9 gives the cycle capture performance of PEI/MCS. It is clear that the cycling stability is poor when the capture-regeneration temperature is 75 ^{o}C. The decay of the capacity might be attributed to the loss of PEI due to the weak interaction between carbon surface and PEI. For other type of supports, such as porous silica, there are strong interactions between amine groups and supports (such as Si-OH groups) [10], which lead to a good cycling stability. In addition, some PEI might be oxidized by the oxygen groups on the surface of MCS during the capture and regeneration, which also caused the loss of CO_2 capacity. The modification of Span 80 did not show improvement for the cycling stability of the material. Although 1,2-epoxybutane decreased the CO_2 capacity of the capture material, it improved the stability. However, obvious loss of CO_2 capacity was also observed during the 9 capture-generation cycles at 75 ^{o}C. It seems difficult to solve the cycling stability of the PEI/MCS at the capture-generation temperature of 75 ^{o}C.

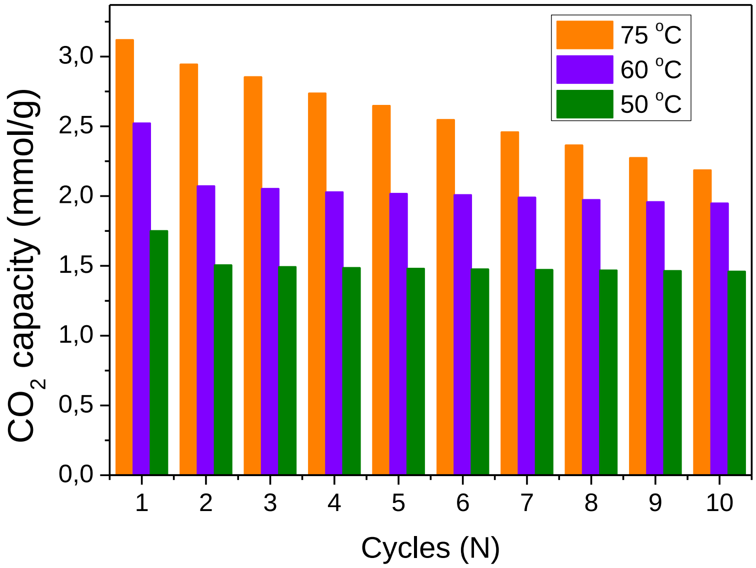

Fig. 10 Stability of the PEI/MCS at different capture-regeneration temperature (capture: 0.05bar CO_2, regeneration: 100%N_2)

We also studied cycling stability of PEI/MCS for CO_2 capture at different temperature, and the results are presented in Fig. 10. The results indicated that decreasing the capture-regeneration temperature, the stability was enhanced significantly. When the capture-regeneration temperature decreased to 50 ^oC, there was almost no CO_2 capacity loss during the 9 capture-regeneration cycles (regeneration >99.5% from the second cycle). From the point of view of cycling stability, 50 ^oC is the best temperature for CO_2 capture for PEI/MCS. Except for CO_2, there are also steam, O_2, SO_x, and NO_x in the tail gas of the natural gas power plant. The steam usually shows a positive role in the CO_2 capture on PEI impregnated porous materials [11,33]. The small contents of O_2 , SO_x, and NO_x might have also effect on the CO_2 capture at 50 ^oC. The effect of steam and other gases on the CO_2 capacity, cycling performance, and CO_2 capture mechanism in PEI/MCS will be studied systematically in next work.

4. Conclusions

In this work, we developed a novel low-concentration CO_2 capture material (PEI/MCS) by loading polyethylenimine (PEI) over mesoporous carbon spheres (MCS). The MCS with perfect spherical morphology were successfully prepared by a hard-template assisted reverse emulsion method. The ratio of silica to carbon (Si/C) in the precursors did not affect the morphology and diameters of MCS, but change the pore structure of MCS significantly. With increasing the Si/C from 0.8 to 1.1, the pore volume of MCS increased from 1.25 to 2.68 cm^3/g. The optimal PEI loadings depending on the pore structure of MCS were 45, 62.5, and 65 wt.% for MCS-0.8, MCS-1.1, and MCS-1.5, respectively. The highest CO_2 capture capacity (3.22 mmol/g) was achieved on 62.5PEI/MCS-1.1 at CO_2 partial pressure of 0.05 bar (5 vol%, a typical concentration of the tail gas from nature gas power plant) and temperature of 75 °C, outperforming most of the solid amine capture materials reported at similar condition. However, the cycling stability is very poor at the capture-regeneration temperature of 75 °C. The promoters Span 80 and 1,2-epoxybutane did not show remarkable effect on the cycling stability of PEI/MCS at 75 °C. Decreasing the capture-regeneration temperature can significantly improve the stability of PEI/MCS, and there is almost no CO_2 capacity loss (regeneration >99.5%) when the capture-regeneration temperature decreased to 50 °C. As a result of high CO_2 capacity and excellent regenerability and stability, PEI/MCS will be one of the ideal candidate materials for CO_2 capture in the future.

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CRediT authorship contribution statement

Qingjun Chen: Experiment, Formal analysis, Writing-original draft, Writing-review & editing. **Siyu Wang:** Experiment. **Kumar Ranjan Rout:** Funding acquisition, Writing - review & editing, Supervision. **De Chen:** Funding acquisition, Writing - review & editing, Supervision.

*Declaration of Interest Statement

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: