Siliceous foam material and its application in post-combustion carbon capture for NGCC plants: effects of aging conditions

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Abstract. In an effort to reduce the overall energy penalty and capital expenditure associated with carbon capture technologies, a variety of porous solid adsorbents have been developed. The limitations of solid sorbent in large-scale process are related to its CO_2 uptake, physicochemical stability, lifecycle, regenerability and operation condition. In this paper, siliceous foam materials were synthesized via a modified microemulsion templating method and functionalized with branched polyethylenimine (PEI). The physical characteristics of synthesized silica adsorbents under different aging conditions were analysed via N2 sorption analysis and Scanned Electron Microscopy (SEM) morphological analysis. CO_2 uptake was evaluated by thermogravimetric analyser (TGA). The results show that CO_2 uptake is desirable even under low CO_2 partial pressure and is predictable with multiple linear regression (MLR) model in the range of examined materials.

1. Introduction

CO_2 emission from large-scale use of fossil fuels is the key drive to global warming [1]. Even though government policies encourage the transition to a more sustainable energy strategy, fossil fuels still dominate primary energy consumption in the worldwide and it is predicted to remain the mainstay of energy source in the future [2]. Carbon Capture and Storage (CCS) is seen as the only approach to mitigate the CO_2 emission while continuing the use of fossil fuels [3]. Post-combustion capture technology, which requires less investment due to the capture system is integrated to the downstream of the existing sites [4] is promoted as a near-term CO_2 abatement strategy since electricity generation is not relied on the presence of CO_2 capture system.

Innovative CO_2 capture technology should keep a beneficial balance between CO_2 capture capacity and energy consumption. Solid adsorption is considered as a feasible substitution to mitigate the energy penalty for state-of-art solvent regeneration process. To date, there are a wide range of solid sorbents being investigated for their ability to capture CO_2, including zeolites [5], metal-organic frameworks (MOFs) [6] and silica gels [7]. However, the application of these physical sorbents is limited, especially for carbon capture at low CO_2 partial pressure.

Previous investigations have demonstrated that amine-modified siliceous materials, either grafting or impregnation, have a great potential in CO_2 adsorption. The CO_2 uptake, however, is highly depended on the pore structure. For example, CO_2 adsorption capacity with 50% PEI is approximately 3.18 mmol/g and 2.03 mmol/g in 15% CO_2/N_2 at 75°C for SBA-15 and MCM-41 respectively [7, 8]. MCF materials, which consists of uniform cells and windows, have a three-dimensional pore system, where the ultralarge cell shape pores (30-50nm) are interconnected by windows with 9-20nm in diameter [9]. Therefore, MCF particles have been the most promising siliceous support materials and have attracted wide attentions in structural modification.

For post-combustion CO_2 capture, large volume of flue gas requires high adsorption capacity and selectivity to mitigate energy penalty. However, partial pressure of CO_2 is even lower in the flue gas from NGCC plants (5% CO_2/N_2) compared to that of coal-fired power plant (15% CO_2/N_2) [10]. Hence, it is worthwhile to promote the sorbents performance, such as CO_2 adsorption capacity, thermal stability, tolerance to impurities and adsorption kinetics. In this study, we investigated the impacts of preparation conditions, particularly aging conditions, on the textual properties of synthesized materials and hence their CO_2 adsorption performance. Mesoporous silica with large surface area, pore volume and pore size, were synthesized to achieve a higher PEI loading, and the performance as CO_2 adsorbents for NGCC plants was evaluated.

2. Material and methods

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2.1 Chemicals

A Nonionic tri-block copolymer surfactant Pluronic P123 (MW_{av}=5800), hydrochloric acid (36%), 1,3,5,-Trimethylbenzene (TMB), tetraethyl orthosilicate (TEOS, 99.999%), ammonium fluoride (NH_4F, 99.99%), branched polyethyleneimine (PEI, MW_{av}=1800). PQ silica was purchased from PQ Corporation.

2.2. Modified microemulsion templating method

The preparation method follows typical route of microemulsion templating reported by Schmidt-Winkel and co-workers[11]. 8g of structure directing agent P123 was dissolved in 23.7g HCl (36%) and 130g deionized (DI) water with continuous stirring at 40°C until complete dissolution. Then 8g TMB was added and the resulting solution was stirring continuously at 40°C. After 2 hours, 18.4ml of TEOS was added and stirred for another 5mins. A hydrolysis step occurred and lasted for 20 hours at 40°C. Thereafter, 9.2mg NH_4F dissolved in 10g deionized water and added to the mixture. The second stage of aging will carried out at 70°C, 80°C, 90°C, 100°C under a static conditions for 15hrs, 24hrs, 42hrs and 53hrs, respectively. The white precipitate was isolated by vacuum filtration and washing with warm DI water. The wet precipitate dried in fume cupboard and calcined in air at 550°C for 8 hours in muffle furnace to obtain final product. The synthesis route is shown in Scheme 1.

2.3.PEI impregnation

PEI loading describes the weight percentage of branched PEI in the impregnated adsorbents as shown in the Eq. (1). The weighted PEI was dissolved in 10ml water with vigorous stirring. After 15mins, calcined silica was gradually poured into the solution. The mixture was stirred overnight at room temperature and then the amine-impregnated adsorbents were dried at 40°C in a vacuum oven for 24hours. The impregnated adsorbents were collected for further testing.

$$PEI\ Loading = \frac{W_{PEI}}{W_{PEI}+W_{support}} \times 100\% \quad (1)$$
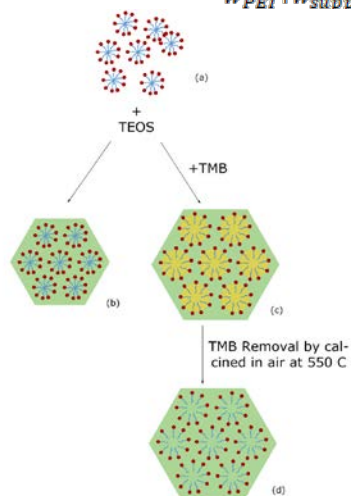
Scheme 1 A typical synthesis route of MCF materials compared to SBA-15.

2.4. Characterisation of silica adsorbents

The nitrogen adsorption-desorption isotherms of silica were examined at 77K with Micromeritics ASAP 2420. The silica was degassed at 120°C for 12 hours before analysis. Surface area values were determined by the Brunauer-Emmett-Teller (BET) equation. In addition, the mesopore volume and micropore volume of the silica were determined using the Barrett-Joyner-Halenda (BJH) method and t-plot equation. The foam materials were coated with gold and the morphology of the sample were obtained using a Zeiss Sigma VP Scanned Electron Microscopy (SEM).

2.5. CO$_2$ uptake

The CO_2 adsorption capacity of the adsorbents was examined by thermogravimetric analyser (Netzsch STA449F3, German). Prior to adsorption experiment, the sample (15-20mg) was preheated to remove any moisture or pre-captured gas by keeping isothermal at 110°C under a nitrogen flow of 50ml/L and then the temperature was set to adsorption temperature which is 75°C. With the aim of testing the availability of PEI impregnated silicas for NGCC power plants, the CO_2 adsorption experiments were implemented with a simulated gas stream of 5% CO_2/N_2 (partial pressure 0.05bar). Each adsorption process keeps isothermal for 60mins to achieve adsorption equilibrium at 75°C. CO_2 uptake was determined through the weight difference between initial dry mass and mass after adsorption as shown in Eq. (2).

$$CO_2 = \frac{W_{final}-W_{initial}}{W_{initial}} \times 100\% \quad (2)$$

3. Results and discussion

3.1. Morphological and pore structural characterisation of synthesized MCF particles

Table 1. Aging conditions and textual properties for PQ-silica and synthesised MCF particles.

Sample	Aging Time (hrs)	Aging Temp. (°C)	Surface Area (m²/g)	Pore Volume (cm²/g)	Pore size (nm)	Cell diameter (nm)	Windows diameter (nm)
PQ-silica	-	-	269.4	1.4	30.0	24.7	18.6
MCF-70-24	24	70	629.3	1.4	13.0	12.7	6.1
MCF-80-24	24	80	558.1	1.6	15.0	15.3	7.8
MCF-90-24	24	90	492.7	1.7	17.0	16.7	10.8
MCF-100-15	15	100	571.4	2.0	18.0	17.9	8.6
MCF-100-24	24	100	554.7	2.1	19.0	19.4	11.0
MCF-100-42	42	100	544.0	2.7	23.0	23.1	13.4
MCF-100-53	53	100	451.3	2.1	22.0	22.0	15.1

Fig. 1 shows the surface morphologies of commercial PQ-silica and representative spherical foams synthesised at different aging conditions. As shown in Fig. 1(a) and (d), due to the formation of spherical TMB/P123 droplets [9], the tubular siliceous foams experience a cylindrical-to-spherical transition, which illustrate the significant increment in pore volume of MCFs as shown in Table 1. In Fig. 1(b) and (c), excessive aggregation of

particles with different sizes is observed in either lower aging temperature (70°C) or limited aging time (15hr). The cluster-like morphologies are somewhat similar to highly-packed disordered PQ-silica[12]. With the increasing of aging temperature from 70°C to 100°C, the particles become larger, more uniform and isolated. With regards to aging temperature, the initial transition follows the same trend as that of aging temperature. However, the aggregation of isolated spherical micelles occurs when aging time increased to 42 hours. When further increasing the aging time to 53 hours, the formation of significantly larger cucurbit-like spherical structure is observed, which implies that the small particles were re-dissolved and aggregated on large particles.
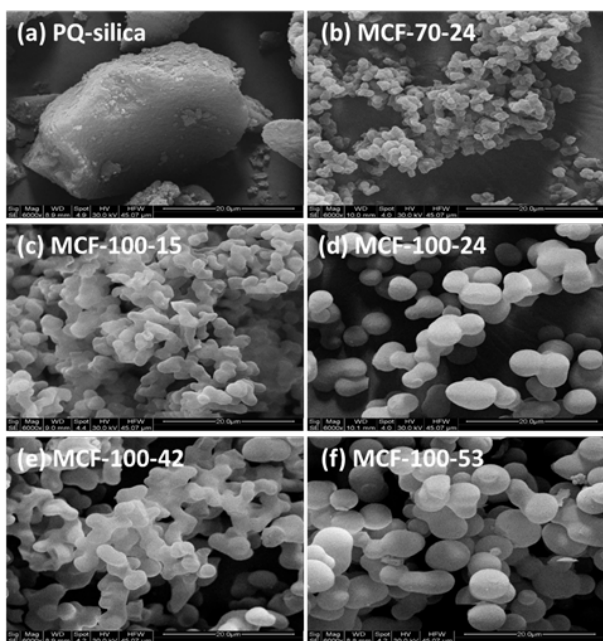

Fig. 1. SEM images of PQ-silica and MCF particles synthesized with different conditions. (a) PQ-silica; (b) MCF-70-24 was aging at 70 °C for 24hours; (c) MCF-100-15 was aging at 100 oC for 15hours; (d) MCF-100-24 was aging at 100 oC for 24hours; (e) MCF-100-42 was aging at 100 °C for 42hours; (f) MCF-100-53 was aging at 100 oC for 53hours.

The N_2 adsorption/desorption isotherms in Fig. 2 are classified as Type IV with steep hysteresis loop, which is typical for a well-defined mesoporous structure [13-15]. In Fig. 2(a) and (b), MCF-100-24 achieved a higher N_2 adsorption than PQ-silica by adding TMB, as also evidenced by SEM images in Fig. 2. Meanwhile, the hysteresis loop of PQ-silica shifted to higher relative pressure region compared with MCF-100-24, which indicts larger pore size. Hysteresis loops of Type H1 indicates a cylinder shaped pores interconnected with narrow windows as shown in Fig. 2(a), 2(b) and 2(d), while the hysteresis loop in Fig. 2(c) tends to be a H2 type that the pore structure is composed of a combination of cylinder and sphere, which implies incomplete transition to spherical structure due to the limited aging time. The analytical results from nitrogen sorption is consistent with observation of SEM, which

illustrate the pore shape is ink-bottle-type [16]. The isotherms in Fig. 2 illustrate that both MCF and modified MCF adsorbents have a more promising substructure than commercial PQ-silica in terms of surface area and pore volume (Table 1). The utilization of TMB brings a phase transformation from highly ordered 1D cylindrical structure to a continuous 3D pore system which comprises uniform spherical cell cavities with identical windows that can further expedite the access to the cavities [9].
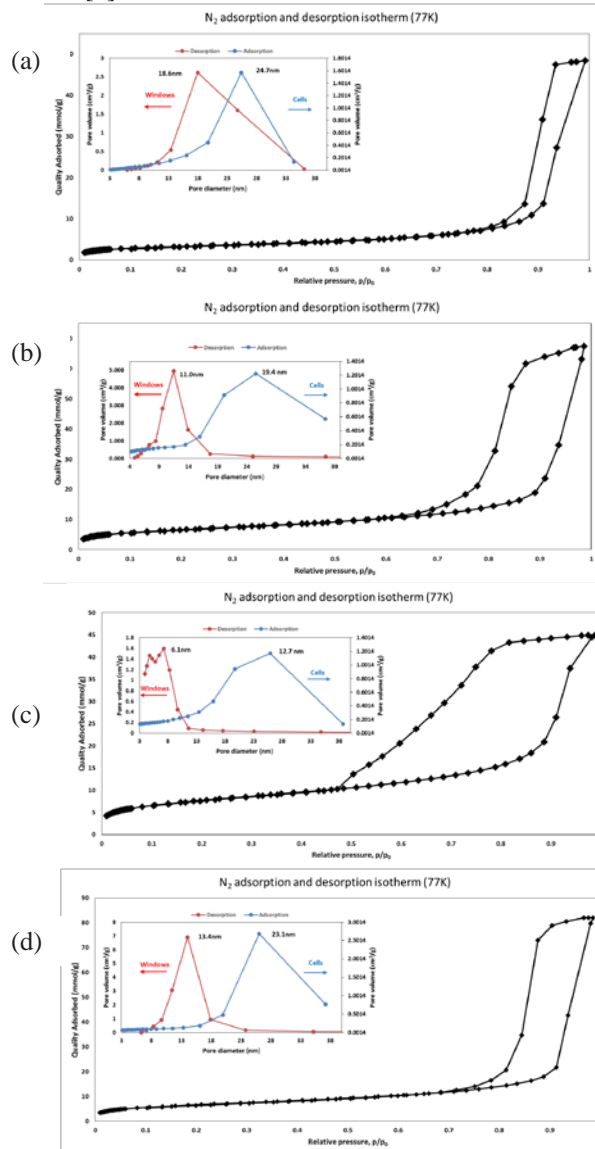

Fig. 2. Nitrogen adsorption/desorption isotherms and corresponding pore size analyses for (a) PQ-silica; (b) MCF-100-24; (c) MCF-70-24 and (d) MCF-100-42 based on a Barret-Joyner-Halenda (BJH) method.

3.2 CO2 adsorption performance

Herein, commercial PQ-silica was used as a baseline to evaluate the CO_2 adsorption performance of synthesized MCFs in this study. As shown in Fig. 3, all PEI-modified MCFs exhibit a higher CO_2 uptake than that of commercial PQ-silica. Due to the limited pore volume, the PEI loading of PQ-silica is only 40wt%, while the MCF particles could achieve 70wt% PEI loading. The MCF-100-42 achieved highest CO_2 uptake

of (16.6wt%) due to its largest pore volume ($2.7cm^3/g$) with cell cavity diameter (23.1nm) as presented in Table 1. Additionally, the results also show that CO_2 uptakes varies even under the same PEI loading. This suggests that porous framework of MCF particles has a significantly influence on the mobility of PEI molecules and hence accessibility of CO_2 within PEI threshold [17, 18]. Although the barrier of CO_2 could be overcome by increasing the adsorption temperature, cycling stability under high adsorption temperature is challenging for PEI-modified adsorbents.
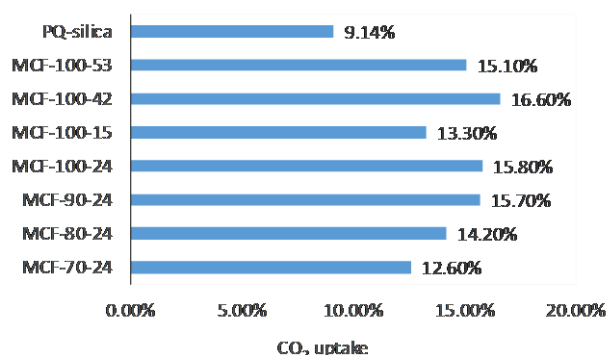

Fig. 3. A comparison of CO_2 uptakes (wt%) of PQ-silica (40wt%PEI) and all synthesised samples (70wt%PEI) at 75°C & 5% CO_2 in N_2.

As discussed above, the CO_2 adsorption capacity is highly depended on pore structure of MCFs, whilst the pore structure could be described by pore volume, pore size, window size and BET surface area. Therefore, it would be beneficial if the CO_2 uptake could be predicted with the parameters above, which in turn, will guide the design of porous framework. In the present work, a multiple linear regression is established via Levenberg-Marquardt training algorithm to investigate how the pore volume (X_v), pore size (X_s) and window size (X_w) relate to CO_2 adsorption capacity (Y). The prediction model (R-squared is 0.98) is shown in Eq. (3), whilst the results given in Fig. 4 shown that prediction model is the model agrees well with the experimental data and vice versa.

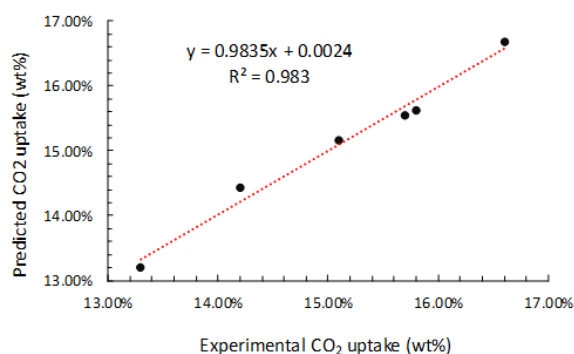$$Y = 0.1903 + 0.1039X_v \pm 0.0219X_s + 0.0149X_w \quad \text{Eq. (3)}$$

Fig. 4. Plot of CO_2 uptake from experimental analysis against the predicted value.

4. Conclusion

The effects of aging conditions on the pore structure of spherical meso-structured siliceous foam materials were investigated. This work demonstrated that the 3D porous framework is tunable with different aging conditions without the addition of any chemicals. The pore volume of synthesized material ranges from 1.4 to $2.7cm^3/g$, whilst pore size is in the range between 13nm to 23nm. In general, higher aging temperature and longer aging period could enhance the growth of cell cavity. In this study, all pore-expanded MCF adsorbents exhibit a higher CO_2 adsorption capacity than that of baseline PQ-silica (SBA-15) with 40wt% PEI loading. The highest CO_2 uptake is 16.6% which is achieved by MCF-100-42 with 70wt% PEI loading. Moreover, the CO_2 uptake of MCF materials is predictable with its pore volume, window size and pore size. This finding could facilitate the design of pore structure to further improve the CO_2 adsorption performance.

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