Mesocellular silica foam supported polyamine adsorbents for dry CO_2 scrubbing: Performance of single versus blended polyamines for impregnation

Xin Liu, Kaixuan Zhou, Matthew Farndon, Edward Meier, Lee Stevens, Hao Liu, Chenggong Sun[*]

Faculty of Engineering, University of Nottingham, Nottingham NG7 2TU, UK

** Corresponding author: cheng-gong.sun@nottingham.ac.uk*

Abstract

Siliceous foams with three-dimensional mesoporous structures were synthesised and used to prepare polyethyleneimine (PEI) and tetraethylenepentamine (TEPA)-functionalised sorbent materials for CO_2 capture, with a particular focus on the performance of impregnated amine blends versus single amine sorbent systems. Using thermal gravimetric analysis supported by other characterisations, the obtained results demonstrated that compared to the impregnated mono-component PEI and TEPA sorbent systems, the binary PEI-TEPA blend sorbents all achieved significantly higher CO_2 capacities and faster adsorption kinetics, due to the enhanced formation of micro-cavities within the supported amine layers that led to reduced CO_2 diffusion resistance and increased accessibility of the amines to CO_2. It was found that at 70 °C and 15% CO_2 in N_2, the CO_2 adsorption capacity of the silica-supported PEI–TEPA (3:2) at 70 wt% amine loading increased by 40% compared to the supported PEI at the same level of amine impregnation, whilst the time to achieve 80% and 90% of the equilibrium adsorption capacity was reduced by 70% and 35%, respectively. Extended cyclic adsorption-desorption tests showed that the TEPA-blended PEI sorbents all exhibited considerably higher thermal stability than both the supported PEI and TEPA sorbents, being indicative of the suppressed urea formation even in the pure and dry CO_2 gas stream used in the desorption cycles. Calculations indicated that compared to the silica-supported PEI sorbents, the higher adsorption capacities achieved by the binary PEI-TEPA sorbent systems could lead up to 10% reduction in the energy requirement for sorbent regeneration, highlighting the suitability of using amine blending as a facile effective strategy to promote the overall performance of polyamine-based adsorbents for CO_2 separation.

Keywords: CO_2 adsorption; adsorption kinetics; mesocellular siliceous foam; polyethyleneimine; TEPA; blended amines

1 Introduction

Carbon capture and storage (CCS) has increasingly been recognised as a necessity, not an option, for achieving net-zero greenhouse gas emissions without threatening global energy security [1, 2]. Amine scrubbing is the state-of-the-art technology for post-combustion CO_2

capture, which shows high capture efficiency of CO_2 even at very low CO_2 concentrations [3, 4], but a combination of its large capital and operating cost, high energy penalty and a range of operational issues have proven to be the major barrier for its wide practical applications in power plants and industries [5, 6]. Techno-economic and environmental assessment studies suggest that CO_2 capture with 30 wt % aqueous MEA solvent can result in up to 80% increase in the cost of electricity for a typical pulverised fuel power plant [7], which can account for 70–80% of the total cost of whole CCS chain [8]. Therefore, exploration of alternative cost-effective capture technologies has been the focus of numerous research activities, with solid adsorbent-based capture technologies also known as dry scrubbing showing sound promise for significantly reduced energy penalty [6, 9]. The Mission Innovation Carbon Capture Innovation Challenge (CCIC) report [10] highlights that revolutionary, not just incremental, advances in cost reduction are needed, and it recommends that among various capture technologies, adsorption-based capture shows the most promise for breakthrough cost reductions if necessary requisites are met with the capture materials. Clearly, the development and deployment of high performing capture materials holds the key to the success of solid adsorbents based capture systems. Among many adsorbents currently under development, amine functionalized solid adsorbents [11] are well recognised as being a class of adsorbents outperforming virtually any other solid adsorbents (e.g. zeolite [12], MOFs [13] and carbon based adsorbents [14-16] in many important aspects, such as their favourable operating temperature windows of 50–80 °C, high CO_2 adsorption capacity and selectivity and fast adsorption rate at low CO_2 partial pressures (<15% v/v), which are the key requisites of capture materials recommended by the CCIC report. It has been reported that a solid adsorbent looping CO_2 capture process, which can be easily facilitated either with circulating fluidised bed or dual fluidised bed technologies, is able to provide breakthrough energy cost reductions of 30-50% or more compared to advanced solvent systems [17].

Instead of using aqueous solution as the carrier, amine functionalized solid adsorbents were prepared by using porous solid substrates, usually mesoporous silica to support the amines. Typically, two main methodologies have been used to prepare amine-based silica adsorbents, one being the grafting method where the CO_2-active amino groups are chemically bound onto the silica support by using linker silanes [18-23] and the other being the method of wet impregnation in which polymeric amines, often polyethyleneimines (PEIs) are physically deposited onto the surface of the porous support, which involves firstly the preparation of the solution of the amines followed by the removal of the solvent used once the wet impregnation is done [24-27]. Compared to amine grafting, the impregnation technique has been more frequently used because of its simplicity, lower cost and ability to upload significantly larger quantities of amines to facilitate higher adsorption capacities [24, 28-32]. Many different types of amines have been used in preparing supported amine adsorbents, such as diethanolamine (DEA) [33], Polyallylamine (PAA) [34], tetraethylenepentamine (TEPA) [35, 36] and polyethyleneimines (PEIs) [37-41]. Among them, PEIs and TEPA are mostly investigated, due to their high thermal stability and adsorption capacity that can be achieved at the desirable adsorption temperatures of 50–75 °C [42, 43]. TEPA-impregnated silica adsorbents benefit from improved adsorption capacity and amine efficiency because of the lower viscosity and higher mobility of the lower molecular mass amine but can suffer from poor thermal stability or amine evaporation loss, which can lead to large losses in CO_2 capacity in a commonly used temperature swing adsorption (TSA) process [30, 44, 45]. In contrast, the polymeric PEIs can maintain much longer lifetime performance due to their high thermal stability, though their CO_2 adsorption rates may not be as good as those of TEPA-based sorbents because of the higher CO_2 diffusion resistance in the more viscous amines [46, 47]. For post-combustion CO_2 capture, the thermal stability of any adsorbents is of paramount importance in determining the ultimate capture performance. As a result, PEIs have been more commonly used in preparing amine-modified adsorbents, and pilot tests at various scales have demonstrated the novel suitability of solid-supported PEI adsorbents for CO_2 capture from both coal-fired and natural gas fired power plants as well as from the air [43, 48].

The energy requirement for sorbent regeneration is another key performance parameter that needs to be considered when selecting sorbent materials for CO_2 capture, and many investigations have been carried out to evaluate the energy requirements of CO_2 capture with supported PEI adsorbents and their relationship with the working capture capacity of the sorbent materials [49-53]. Sjostrom and Krutka [51] evaluated the regeneration energy requirement of different types of PEI adsorbents, and they found that the energy requirement was sharply reduced from 4.3 to 2.6 GJ/tCO_2 when the working capacity increased from 0.652 to 1.59 mol/kg under same sorbent regeneration conditions. The investigation by Zhang et al [53] revealed that working capacity was one of the most influential factors that impact the regeneration energy requirement of a sorbent material, and it shows that the regeneration energy was decreased from 2.46 to 2.18 GJ/tCO_2 when the working capacity increased from 1.35 to 2.03 mol/kg, which was much lower than the 3.9 GJ/tCO_2 obtained for typical MEA systems and 3.3 GJ/tCO_2 for advanced MEA systems. All the above works highlighted the importance of CO_2 adsorption capacity in reducing the overall energy penalty of CO_2 capture. Higher adsorption capacity could reduce the mass of sorbents used for each unit of CO_2 captured, which will reduce the sensible heat required to heat up and cool down the adsorbents in a temperature swing process [50]. In addition, high adsorption capacity can also minimize the usage of sorbent and therefore reduce the auxiliary energy requirement to circulate the sorbent materials in the adsorption and desorption cycles.

Therefore, a key research focus has been to boost the CO_2 adsorption capacity of polyamine-based sorbent materials by maximising the amine loading whilst reducing the mass transfer limitations of adsorption [23]. One of the most important strategies that have been examined has been the development of new porous silica supports with large pore volumes and pore sizes. Numerous studies have found that the adsorption capacity of supported amine adsorbents increased with pore size and total pore volume [35, 36, 41]. Amine sorbent materials prepared using silica supports with larger pore sizes and greater pore interconnections, such as MCF [29], KIT-6 [37] and mesoporous silica capsules (HMS) [40], were found to exhibit much higher adsorption capacities than those prepared with SBA-15 [23], MCM-41[38] and MCM-48 [39] as the porous support. Efforts have been made to improve the accessibility of supported amines to CO_2 and hence to reduce CO_2 diffusion resistance by introducing dispersants or diffusion promoters into the bulk amines during wet impregnation. Non-amine surfactants, such as PEG[54-59], SPAN 80 [58] and CTAb [58, 60, 61] and lower molecular mass amines, such as triethanolamine (TEA) [61], monoethanolamine (MEA) [62], diethanolamine (DEA) [62, 63], 3-(aminopropyl)triethoxysilane (APTES) [64, 65, 66] have been investigated. Meth et al [56] studied the effect of PEG addition on the adsorption performance of PEI (M_n ~25000) impregnated fumed silica sorbents, and they found that the presence of PEG could improve both the adsorption capacity and amine efficiency of the PEI sorbents due to sharply reduced diffusional limitations of CO_2 in the bulk phase of the supported PEI, with the optimal adsorption temperature decreased from 80 °C to 50 °C before and after PEG addition. The research by Tanthana and Chuang [59] revealed that two types of CO_2 adsorption exist in PEG-doped PEI adsorbents, including the strongly adsorbed CO_2 via carbamate formation and the weakly adsorbed CO_2 due to the intermolecular hydrogen bond formed between the PEG and amine groups (NH_2-O). The weak CO_2 adsorption due to hydrogen bonding decreased with increasing adsorption temperature, which may account for the decrease of amine efficiency with temperature observed by Sakwa-Novak et al [57]. In addition to PEG, other dispersing surfactants, such as P123, F127 and Span80 were also studied [58, 60]. For instance, Wang et al [58] found that all the sorbent materials mediated with the additives showed higher CO_2 adsorption capacities than their non-mediated counterparts, with Span 80 showing the best performance where an 26% increase in CO_2 capacity was obtained for the PEI sorbents mediated with 7 wt% SPAN 80. The findings suggest that the co-impregnation of surfactants can enable the creation of additional CO_2 pathways or channels within the bulk phase of the supported polyamines, which helps reduce the CO_2 diffusion resistance and improve the accessibility of the amine groups to CO_2, whilst the hydroxyl groups present in some of the surfactants examined may be able to mediate the interactions between CO_2 and amine groups to enhance the CO_2 adsorption [59].

However, it is noteworthy that there may exist limitations for using surfactant co-impregnation to improve the adsorption performance of supported polyamine adsorbents, because firstly it may not necessarily be able to increase the CO_2 adsorption performance at practical flue gas temperatures [57, 58]; secondly, the co-impregnation of surfactants, which are mostly hydroscopic, can potentially increase significantly the co-adsorption of moisture and hence increase the regeneration energy requirement [54]; and thirdly, the sorbent preparation cost can be considerably increased as it usually involves the use of secondary organic solvents to dissolve the surfactants [58] or pre-treatments the original sorbents e.g. ethanol extraction [61].

Some low molecular mass amines may serve the same role but without the common issues with the surfactants used for co-impregnation. Dao et al. [62] examined a range of different types of low molecular weight amines (e.g. TEPA, TEA, DEA, MEA, PZ) for preparing supported mixed amine sorbent materials by wet impregnation, and it was found that the silica sorbent prepared with 40 wt% TEPA and 30 wt% DEA showed the highest CO_2 uptake of 5.91 mmol/g at 50 °C and 1 bar CO_2, which was believed to be attributable to the DEA-contained hydroxyl groups that can improve the mobility of the amines whilst also stabilize the carbamate anion through hydrogen bonding. However, despite the synergistic effect observed, the supported low molecular weight amines blend sorbents may have lifetime performance issues due to the potential significant evaporation losses that may occur at relatively high adsorption and desorption temperatures, although no cyclic adsorption-desorption tests were performed in the investigation by Dao et al [62]. Fauth et al. [66] found that the silica-supported PEI sorbents mediated with 3-(aminopropyl)triethoxysilane all showed higher capacities and amine efficiencies with excellent cyclic performances than the non-mediated ones at different CO_2 partial pressures, highlighting the suitability of using relatively lower molecular mass amines to mediate the polymeric PEI-based CO_2 capture materials. To date, the majority of investigations on supported polyamines for CO_2 capture have been focused on developing more porous support materials as a means to maximise the amine loading, whereas investigations into effective amine blending strategies, which can be used to improve the mobility and accessibility of supported viscous polymeric amines during CO_2 adsorption, have been very limited to date. In this study, a series of mesocellular siliceous foam (MCF) materials with different pore sizes were synthesized and used as the support to prepare supported PEI blend capture materials, and TEPA instead of surfactants or other low molecular weight amines was used as the substitute of promotor to prepare the blended PEI adsorbents. Based on the performance data of the new adsorbent materials, the energy performance of the materials for CO_2 capture with circulating fluidised bed were assessed.

2 Experimental

2.1 preparation of MCF silica and amine-modified silica adsorbents

In this research, all chemicals were obtained from Sigma-Aldrich, including Pluronic P123 (EO_{20}-PO_{70}-EO_{20}, MW_{av} = 5800), HCl (37%), 1,3,5-trimethylbenzene (TMB), tetraethyl orthosilicate (TEOS, 99.999%), ammonium fluoride (NH_4F, 99.99%), TEPA and branched PEI with an average molecular weight of 600. The mesoporous cellular silica foam with 3D interconnected pore structures were prepared via the microemulsion templating method as reported by Schmidt-Winkel [67]. In a typical process, 8g of Pluronic P123 and 20.1ml of 37wt% HCl were mixed with 130 ml deionized water at 40 °C. After P123 was completely dissolved, a calculated amount of TMB as the pore-expanding agent was added to the solution. Following 2 hours of stirring at 40°C, 18.4 ml of TEOS were added to the mixture and the resultant solution was then kept at 40 °C for 20 hours. Then 92 mg of NH_4F was dissolved in 10g of water and added to the solution before it was left to ageing at selected different temperatures for 24 hours. The white precipitate formed was then separated by centrifuging and dried in atmospheric conditions. The dried precipitate was then calcined at 550 °C for 8 hours in air. For easy comparison, the samples prepared with a fixed TMB/P123 ratio of 1:1 at the different aging temperatures of 100, 120 and 160 °C were labelled as MS-1, MS-2, MS-3, respectively. The sample prepared with a TMB to P123 ratio of 1:3 at 100 °C was labelled as MS-4.

To prepare the amine functionalized MCF adsorbent materials, a typical facile wet impregnation method was used. For a given target level of amine loading, calculated amounts of PEI, TEPA or binary TEPA-PEI mixtures were first dissolved into 10 ml water under constant stirring conditions, and the corresponding amount of MCF silica was then added into the aqueous amine solution. After overnight stirring, the aqueous mixture was then dried at 40 °C in a vacuum oven for 24 hours to obtain the supported amine sorbent materials.

2.2 Characterization of MCF materials

The textural properties of the MCF materials synthesised were characterized by using N_2 sorption isotherms at 77 K with a Micrometrics ASAP 2420 instrument. In each measurement, the samples were first degassed at 120 °C for 16 hrs before the measurement. Surface area was calculated by using the Brunauer-Emmett-Teller (BET) method, while the Barrett, Joyner, and Halenda (BJH) method was used to determine the pore size and window size. The whole range pore size distribution was determined by the density functional theory (DFT) method.

A JEOL 7100F Field Emission Gun Scanning Electron Microscope (FEG-SEM) (JEOL USA, Inc.) was used to study the morphology of the MCF samples. Fourier-transform infrared spectroscopy (FTIR) analysis was performed using a Bruker Tensor-27 FT-IR Spectrometer. The spectra were recorded in the 4000–400 cm^{-1} region.

2.3 Characterization of amine-modified MCF adsorbents

The CO_2 adsorption performance of amine modified MCF adsorbents was characterised by using a thermogravimetric analyser (TGA Q-500) in a simulated flue gas stream containing15% CO_2 in N_2. For each adsorption test, about 15 mg adsorbent was first dried at 110 °C in a flow of nitrogen (100 ml/min) for 30 min, and the adsorbents was then cooled down to 70 °C for CO_2 adsorption with the gas switched to 15% CO_2 in N_2 at a flow rate of 100 ml/min. In order to investigate the stability and regenerability of MCF-supported amine sorbents, cyclic adsorption-desorption test of selected samples was also conducted. In each cycle, the sample was first kept at 70 °C in simulated flue gas for 10 min for adsorption, and then the adsorbent was heated up to 100 °C and kept at this temperature for desorption for 10 min with the gas switched to N_2 before it was allowed to cool down to 70 °C to start another cycle.

3 Results and Discussions

3.1 Textural properties of mesoporous silica support

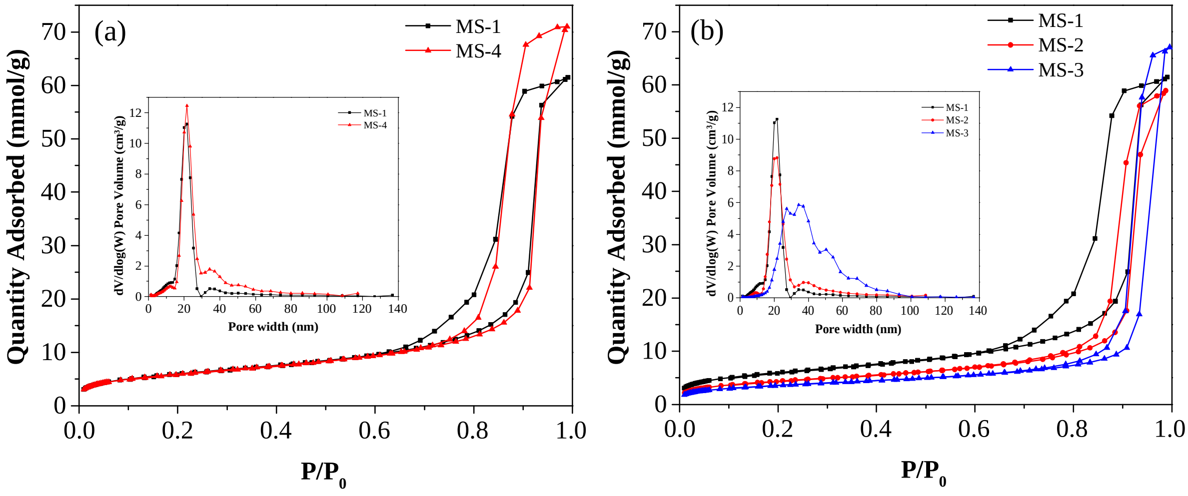


Figure 1 Nitrogen adsorption isotherms and pore size distribution (PSDs) of MCF prepared under different conditions

Figure 1 shows the nitrogen adsorption-desorption isotherms and pore size distributions of the porous MCF samples synthesized under different conditions. It can be seen that all MCF samples had typical type IV isotherms with narrow type H1 hysteresis loops in the high relative pressures (P/P_0) region, which is characteristic of mesoporous materials with large accessible mesopores of high pore size uniformity and pore connectivity [68]. It is evident that with increasing TMB/P123 mass ratio (Fig. 1a) or aging temperature (Fig. 1b), the sorption hysteresis loop became narrowed and shifted towards higher relative pressure regions with increasing amount of nitrogen being adsorbed, indicating the formation of larger and/or increasingly more ordered mesopores or even macropores. The results show that compared to the TMB/P123 ratio, the aging temperature appears to have a larger impact on the pore structure of the MCF materials synthesised. As shown in Fig. 1b, a slight increase in the aging temperature from 120 to 160 °C led to the formation of significantly larger meso or even macropores with wide pore size distributions, whereas no significant changes in pore size distributions were observed as the TMB/P123 ratio was increased from 1 to 3. This suggests that though higher TMB concentrations and aging temperatures both can enhance silica condensation as a result of accelerated hydrolysis of TEOS, aging temperature plays a more important role in the aggregation of smaller silica micelles to form larger particles, giving rise to wider pore size distributions with less ordered pore structures.

Table 1 Specific Surface Areas and Pore Structure Parameters of the MCF samples

	BET Surface Area (m^2/g)	**Pore Size (nm)**	**Window Size (nm)**	**V$_{Meso}$ (cm^3/g)**	**V$_{total}$ (cm^3/g)**
MS-1	492	19.8	13.0	2.04	2.08
MS-2	360	25.7	19.2	1.94	2.02
MS-3	294	33.6	25.1	1.96	2.26
MS-4	487	23.4	15.1	2.30	2.40

Table 1 summarizes the surface textural properties of the MCF samples derived from nitrogen sorption isotherms. As expected, the surface area decreased as total pore volume increased, due to the formation of larger pores with larger pore window sizes with increasing aging temperature and TMB/P123 ratio. An increase in the aging temperature from 100 to 160 ^{o}C was found to lead to a sharp decrease in the surface area of the MCF materials from 492 to 294 m^2/g while the total pore volume of the materials was increased from 2.08 to 2.26 cm^3/g. Similar but more moderate trend was observed when TMB/P123 ratio was increased from 1 to 3. Clearly, compared to the TMB/P123 ratio, the aging temperature seems to play a significantly greater role in the formation of larger pores. For instance, as shown in Table 1, the pore diameter and pore window size of the MCF sample synthesised with a TMB/P123 ratio of 1 was significantly expanded from 19.8 to 33.6 nm and 13.0 to 25.1 nm, respectively as the aging temperature increased from 100 to 160 ^{o}C. This highlights the novel pore expanding effects of aging temperature.

Figure 2 shows the morphologies of MCF samples prepared under different conditions. MS-1 prepared at 100 ^{o}C and TMB/P123 ratio of 1 exhibit almost uniform spherical morphology. When increasing the aging temperature from 100 to 160 ^{o}C, the spherical silica particles with reduced size tend to assemble into larger particular aggregates. In contrast, aggregation did not occur by changing TMB/P123 ratio but a transformation from spherical to large ellipsoidal particles was evident with increasing TMB/P123 ratio from 1 to 3 at 100 ^{o}C. The SEM imaging of the MCF particles at high magnifications reveals that all silica samples have 3D-interconnected open polygonal networks framed by silica struts (Figure S1), highlighting the typical characteristic structural feature of the MCFs.

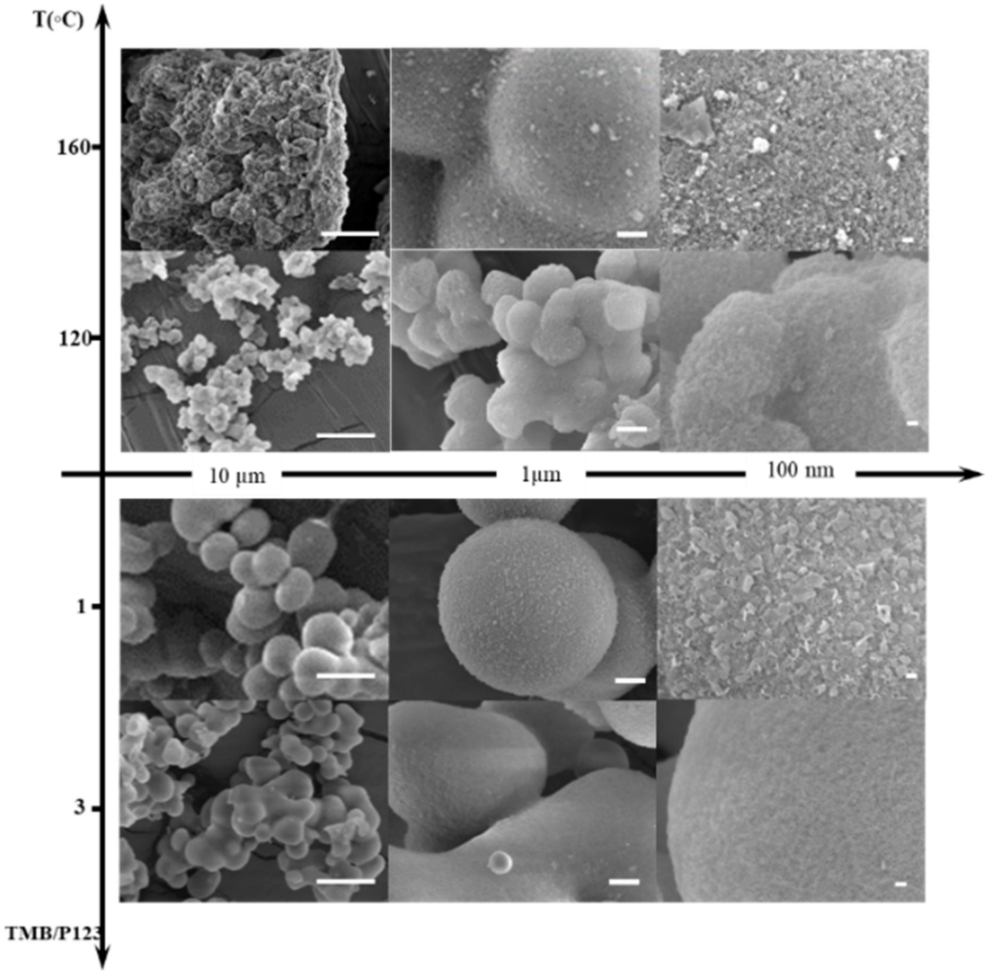
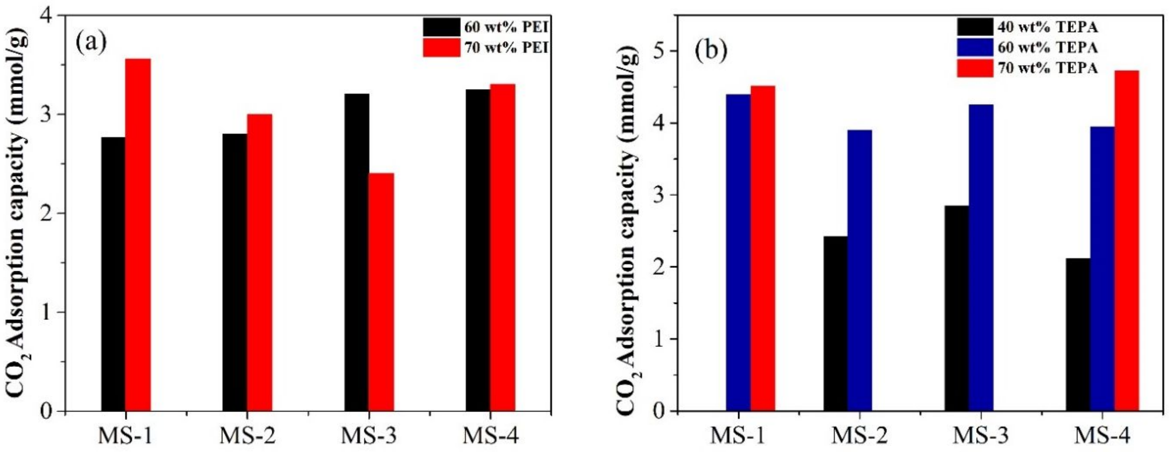


Figure 2 Morphology of the MCFs synthesized under different preparation conditions

3.2 CO_2 adsorption performance

3.2.1 CO_2 adsorption performance of PEI/TEPA modified MCF materials



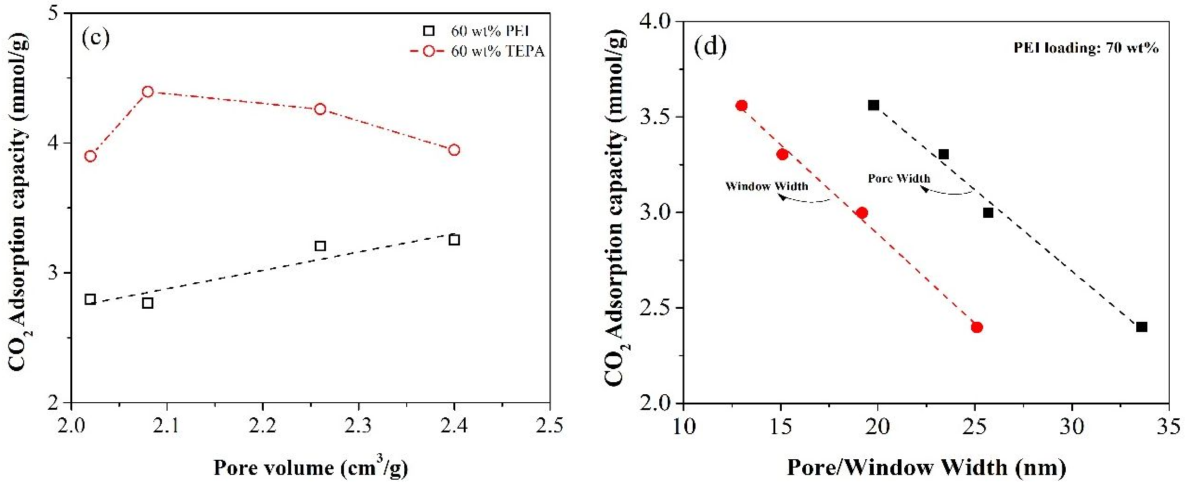


Figure 3 Adsorption performance of TEPA and PEI individually modified MCF adsorbents and its relationship with the surface textural properties of the MCF supports a, b: CO_2 uptake of amine modified MCFs at 70 ^{o}C and 15% CO_2 in N_2; c, d: the relationship between CO_2 adsorption capacity and total pore volume, pore and window size of MCF supports.

Figure 3(a, b) shows the CO_2 uptake of the MCF sorbent materials prepared with different loading levels of individual PEI and TEPA. The CO_2 adsorption capacity was measured at 70 ^{o}C in 15% CO_2 balanced with N_2. It can be seen that all the amine modified MCF adsorbents showed increased CO_2 capacity with increasing levels of amine loading but significant variations in CO_2 uptake are evident, which appears to be determined by the surface textural properties of the silica support used. At a PEI loading level of 70 wt%, MS-1 gave rise to the highest adsorption capacity of 3.60 mmol/g, followed by MS-4 that yielded a capacity of 3.31 mmol/g. However, at a lower PEI loading level of 60 wt% g, the highest CO_2 adsorption capacity of 3.25 mmol/g, was obtained for MS-4 prepared with the highest PMB/P123 ratio of 3 but at the lowest aging temperature of just 100 ^{o}C. In comparison with PEI, the impregnation of TEPA was found to lead to generally higher CO_2 uptakes for all the MCF materials at the same loading levels, as shown in Figure 3b. At a TEPA loading level of 70 wt%, the MCF sample MS-4 achieved the highest CO_2 adsorption capacity of 4.73 mmol/g among all the MCF samples, which was over 30% higher than the highest capacity of 3.60 mmol/g achieved by the MCF-supported PEI sorbents. The higher CO_2 adsorption capacity obtained for the supported TEPA sorbents is clearly due to the considerably higher content of primary and secondary amino groups present in TEPA compared to the branched PEIs that also contain significant quantities of tertiary amine moieties, which could represent up to 20-35% of total amino groups in PEI depending on the branchedness of different PEIs. The tertiary amine groups present in the PEIs are generally unreactive towards CO_2 under dry conditions, as their reactions with CO_2 require the essential participation of water [44]. In addition, the higher CO_2 uptake observed for the supported TEPA might also benefit from the lower viscosity and molecular mass of TEPA, which can give rise to higher molecular mobility and the accessibility of the amine groups for improved CO_2 adsorption performance [30]. A comparison with similar previous investigations as shown in Table 2 shows that the CO_2 uptake is significantly higher than those of many, if not all, of the best-performing supported PEI and TEPA adsorbent materials.

The results also reveal that for both TEPA and PEI impregnation, there appears to exist an optimal or maximum amine loading level, which varied considerably for different MCF materials examined because of their different textural properties. It was found that beyond the optimal level, further increase in amine loading could only lead to marginal or negligible increases in CO_2 uptake for most of the MCF samples (e.g. MS-4 for PEI and MS-1 for TEPA impregnation) whilst for some MCF samples (e.g. MS-3 for PEI and TEPA impregnation), it could cause sharp decreases in CO_2 capacity, and this highlights the effect of the textural properties of MCF materials on their performance for amine impregnation. The findings are consistent with previous studies on TEPA or PEI impregnation [62, 70].

Table 2 Comparisons of the performance of amine-Impregnated mesoporous silica

Support	Amine type	CO_2 partial pressure (bar)	CO_2 adsorption capacity (mmol/g)	Ref.
MS-1	PEI	0.15	**3.60**	**This work**
MS-4	TEPA	0.15	**4.73**	**This work**
MCM-41	PEI	0.15	2.97	[26]
MCM-41	PEI	0.15	2.02	[55]
SBA-15	PEI	0.15	3.18	[24]
SBA-15	PEI	0.15	2.40	[69]
KIT-6	PEI	0.15	1.95	[41]
KIT-6	,PEI	1	3.06	[71]
MCF	PEI	0.15	4.10	[29]
MCF	PEI	0.15	3.45	[72]
MCF	PEI	0.15	3.10	[42]
KIT-6	TEPA	0.10	3.20	[73]
SBA-15	TEPA	1	3.93	[74]
MCM-41	TEPA	0.15	2.45	[62]
MCF	TEPA	0.1	4.56	[36]
MCF	TEPA	1	4.50	[75]

Figure 3 (c, d) show the variation of CO_2 uptake as a function of the textural properties of the MCF materials. It is evident that the adsorption performance of the supported amines was determined by both the type of the amines for impregnation and the textural properties of the MCF supports. At an amine impregnation level of 60 wt%, as shown in Fig. 3c, a linear relationship was obtained between the CO_2 uptake of the supported PEI and the total pore volume of the MCF support materials, which agrees well with previous investigations [29, 49, 72, 76]. For TEPA impregnation, however, there appeared to exist an optimal or maximum pore volume beyond which further increases in pore volume was found to cause sharp decreases in CO_2 uptake, which is consistent with the observation that most of the MCF-supported TEPA sorbents became pasty when the TEPA content reached 70 wt%. It is generally believed that the larger the pore volume that a porous support can have, the more amines can be accommodated and hence higher CO_2 uptake can be achieved [49, 72, 75]. While this presumption could be generally applicable to the impregnation of higher molecular mass amines despite the potentially deceased amine efficiencies, it may not necessarily hold in the case of the impregnation of low molecular mass amines (e.g. TEPA and other lower molecular weight amines). Based on the above results, it can be reasonably inferred that for impregnation of low molecular mass amines, too large a pore size or volume, which are usually at a large cost of supporting surface areas (Table 1), can lead to the formation of ponding amines or emergence of amine ponding effect due to excessive accumulation of unsupported amines, giving rise to dramatically reduced overall accessibility of the amines and hence decreased CO_2 capacity with increasing impregnation levels of lower molecular amines.

Meanwhile, correlation analyses revealed that the CO_2 uptake of the supported PEIs decreased linearly with increasing pore size and pore window size of the MCF supports (Fig. 3d) when impregnated with 70 wt% PEI, indicating the deceased accessibility of the supported amines as the amine layer was destined to become thicker with increase in the pore/window size at a cost of the surface area (Table 1). However, no evident relationship was found at 60wt% PEI and for TEPA, both at 60 and 70 wt% loading levels. This suggests that the importance of the pore/window size of a given porous support in determining the CO_2 capacity or amine efficiency of its supported amines can vary significantly with the type of amines for impregnation and the levels of amine loading.

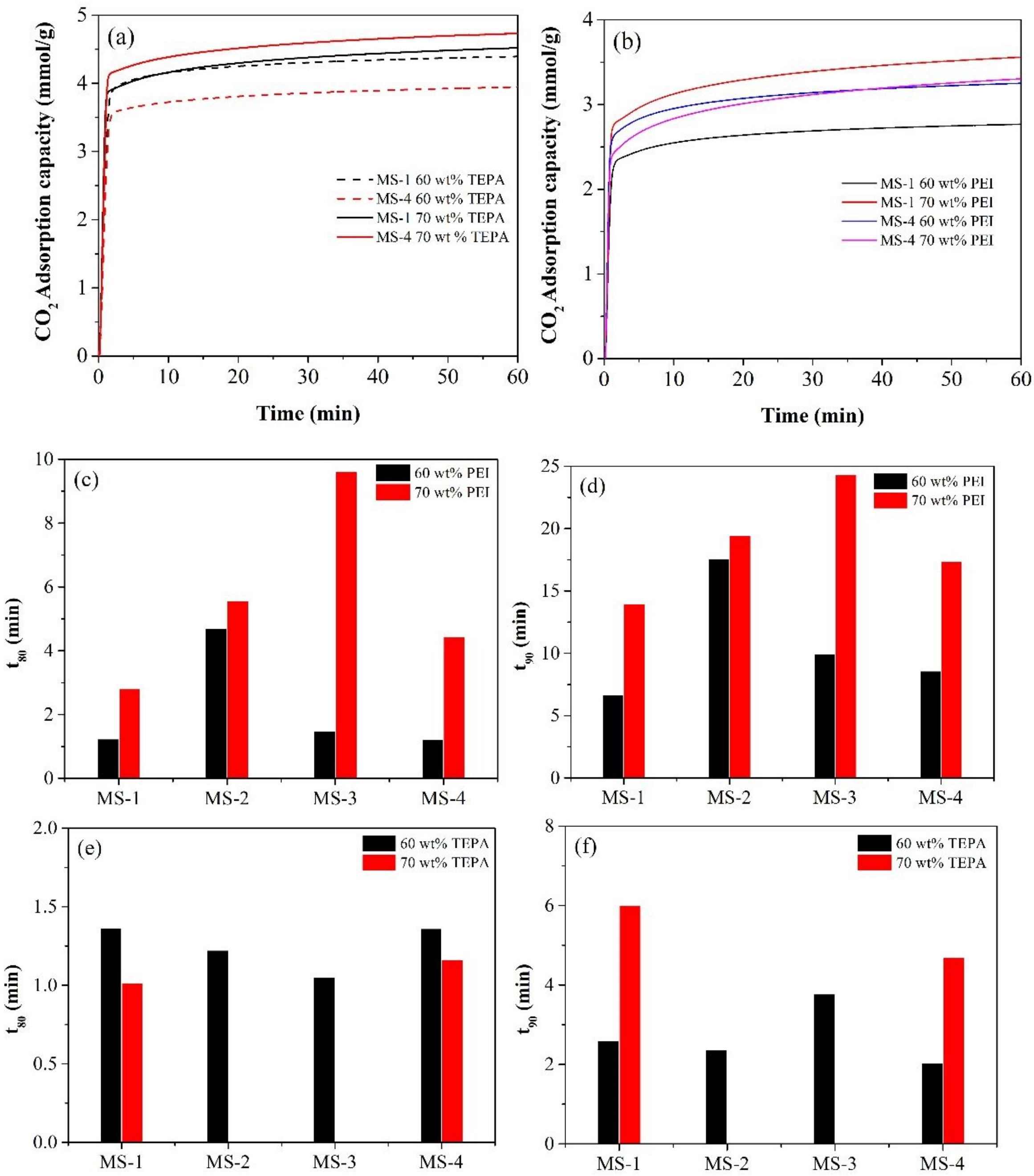


Figure 4 CO_2 adsorption kinetics of MCF-supported TEPA and PEI adsorbents a, b: TGA adsorption profiles at 70 °C and 15% CO_2 in N_2; c-d: time to achieve 80% and 90% of the equilibrium adsorption capacity

Figure 4 shows the CO_2 adsorption kinetics and the times taken to reach 80% and 90% of equilibrium adsorption capacity for different MCF-supported sorbent materials. It can be seen from Figure 4(a, b) that the CO_2 adsorption on amine-modified MCF samples appears to follow a two-stage process: a sharp linear CO_2 uptake within the first few minutes of adsorption, followed by a slow adsorption process where the sorbent materials could only achieve marginal increases in CO_2 uptake over a prolonged period of adsorption, the latter being more indicative of the changing CO_2 diffusion resistance within the phase of supported amines during CO_2 adsorption [77, 78]. As the amount of CO_2 adsorbed by the amine increased, the viscosity or density of the supported amine phase also increased due to the formation of salt bridges and/or hydrogen bonded networks of amine-CO_2 zwitterions or carbamates, resulting in increased CO_2 diffusion resistance [79-81]. The adsorption kinetics were further evaluated by comparing the times taken to achieve 80% (t_{80}) and 90% (t_{90}) of the equilibrium adsorption capacity for different sorbent materials, as shown in Figure 4 (c-f). It can be seen that the t_{80} and t_{90} both varied not only with different silica supports but also with the type and loading level of the amines used for impregnation. It was found that the PEI and TEPA sorbents prepared with the MS-3 support, which had the largest pore size and lowest surface area (Table 1), showed the longest t_{80} and t_{90}, highlighting the high CO_2 diffusion resistance arising from the greatly increased thickness or reduced accessibility of the amine layer as a result of the low surface area of this porous support. In general, all the supported-TEPA sorbents were found to exhibit significantly faster CO_2 adsorption rates, as shown by their t_{80} and t_{90} which were up to 4 times shorter than those of the supported PEI sorbents in the same conditions, as shown in Fig. 4(c-f). This is clearly due to the higher content and lower steric hindrance of the primary and secondary amine groups in the supported TEPA molecules, compared to the PEI molecules. In addition, the amount of amine impregnated is another important factor affecting the CO_2 adsorption kinetics. It can be seen that all the MCF-supported PEI and TEPA sorbents were able to quickly achieve 80% of the equilibrium CO_2 capacity in 1-5 minutes but it could take up to 25 min for the sorbents to reach 90% of equilibrium capacity particularly at high amine impregnation levels, indicating the increasing mass transfer resistance as more CO_2 is adsorbed and the CO_2 molecules migrated deeper into the amine layer.

When the adsorption capacity and kinetics are both taken into account, the porous silica, MS-1, which has the largest surface area of 492 m^2/g with the smallest pore size (19.8 nm) and pore window size (13.0 nm) appears to be the best performing support for TEPA impregnation, whereas MS-1, which has a slightly lower surface area but with larger pore size (23.4 nm) and window size (15.1 nm) than MS-4, is instead the most favourable for supporting the polymeric PEI.

3.2.2 CO_2 adsorption performance of blended amines modified MCF materials

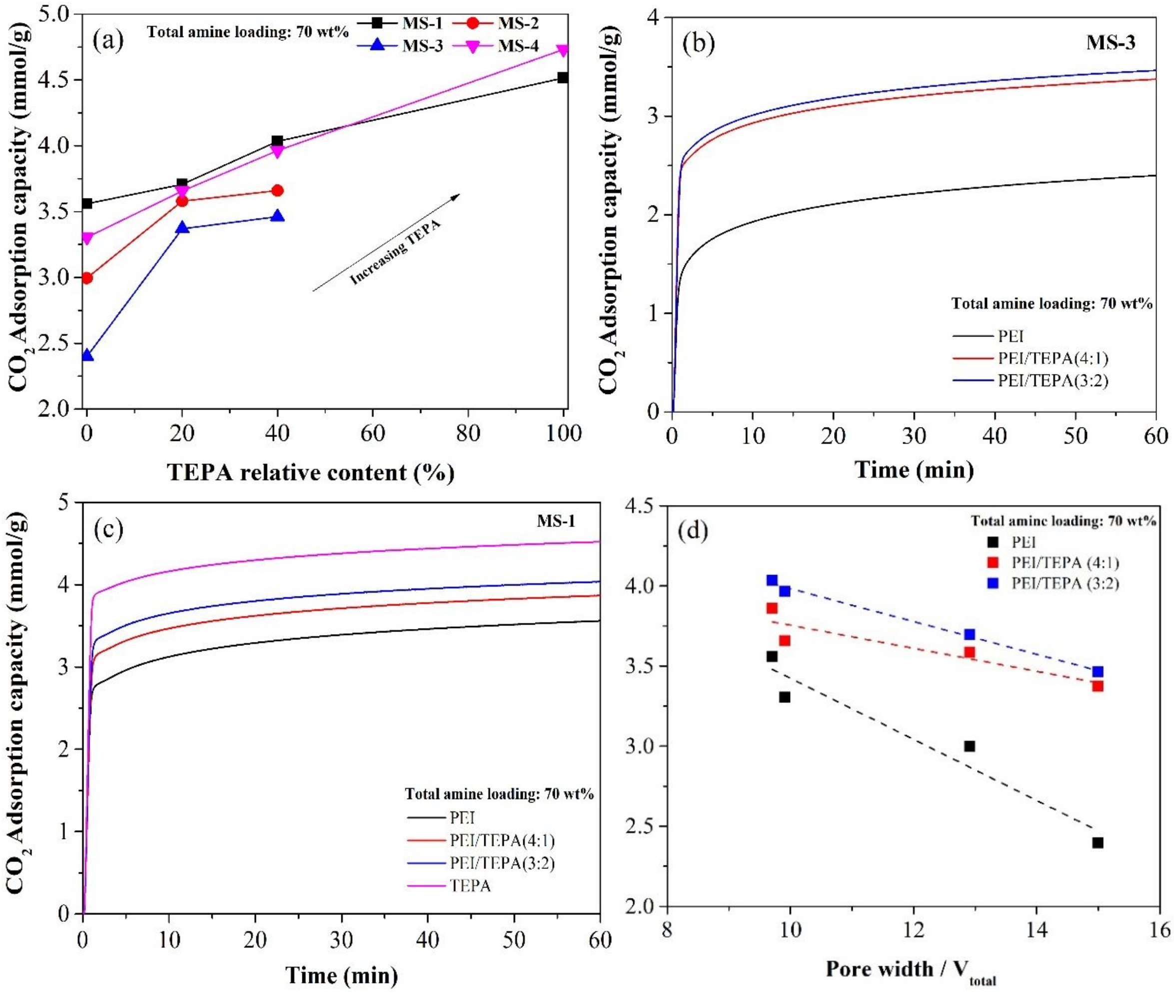
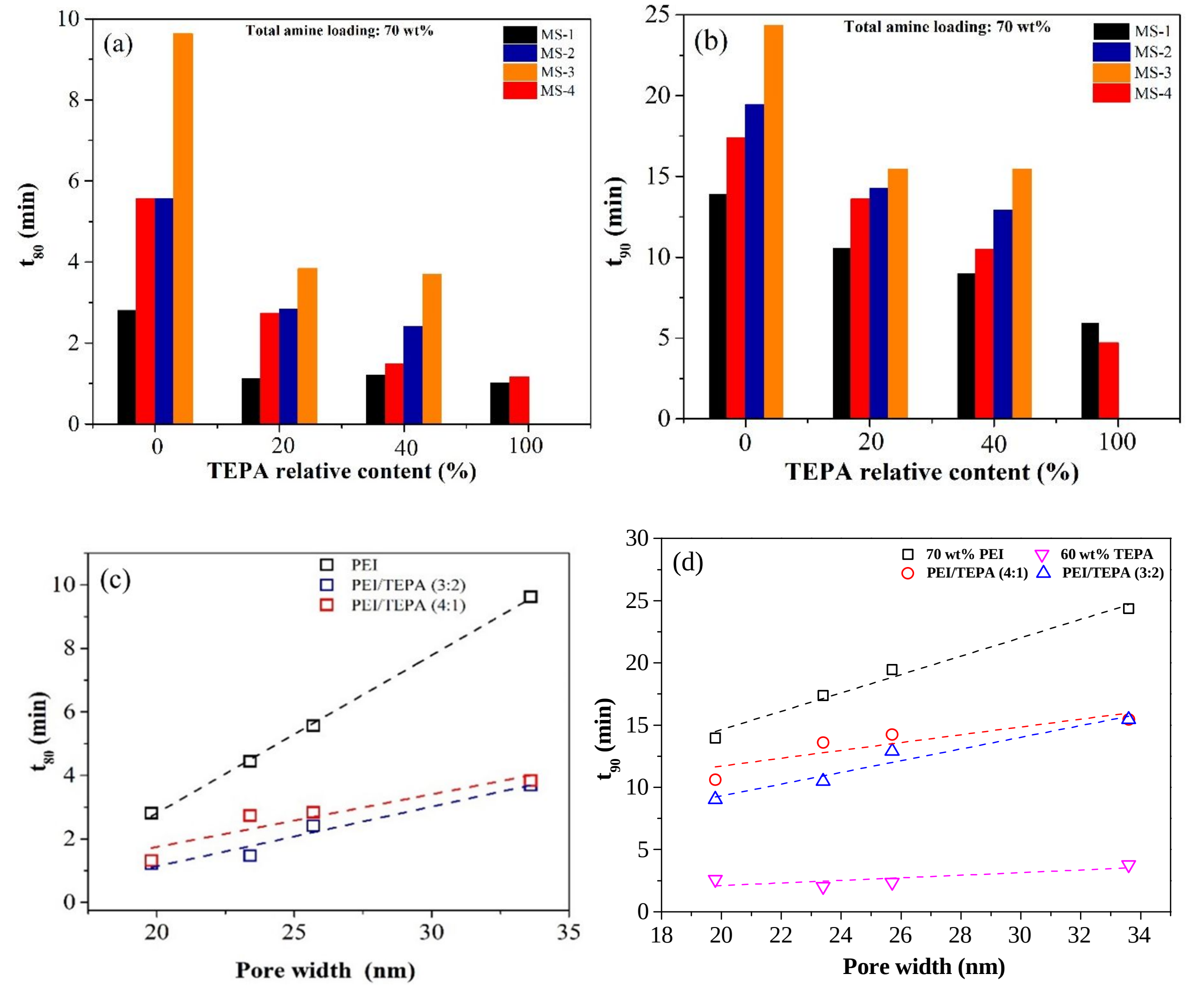


Figure 5 CO_2 adsorption performance of binary amine (PEI-TEPA) modified MCF adsorbents at 15% CO_2 in N_2 and an adsorption temperature of 75 ^{0}C.
(a) adsorption capacity of the supported binary TEPA/PEI sorbents with different relative TEPA content (total amine loading 70 wt%); (b-c): adsorption profiles for TEPA, PEI and binary PEI/TEPA sorbents; (d): the relationship between the CO_2 adsorption capacity and the pore volume and size of the silica support

The results above demonstrate that TEPA with low viscosity and good mobility exhibited significantly better performance than PEI, in terms of both the adsorption capacity and kinetics. However, the relatively low boiling point of TEPA may pose a challenge to its robustness and longevity in practical applications. In this study, we examined the suitability of using TEPA to improve the overall performance of PEI-based sorbents for CO_2 capture, with an expectation that the two amines would complement each other in the binary sorbent system. Figure 5 displays the CO_2 adsorption performance of the MCF-supported binary amine sorbent materials. It can be seen that that at a 70 wt% loading level of the amine mixture, the binary amine adsorbents all achieved significantly higher CO_2 uptakes than the supported PEI, with

CO_2 adsorption capacity increasing almost linearly with increase in the relative content of TEPA in the binary mixture. As shown in Fig. 5a, the MS-1 supported binary amine mixture showed the best performance and the CO_2 capacity reached 4.03 mmol/g at a PEI/TEPA mass ratio of 3:2, which was 12% higher than that of the supported PEI (3.60 mmol/g) and represents one of the highest reported so far under similar conditions (Table 2). The largest improvement, however, was observed for the binary amine modified MS-3 where the CO_2 capacity increased by 40% to 3.37 mmol/g for 20% TEPA co-impregnation (PEI/TEPA = 4:1), and by 45% to 3.46 mmol/g when the impregnation was increased to 40% (PEI/TEPA = 3:2), respectively, compared to the 2.40 mmol/g obtained for the PEI at the same loading level.



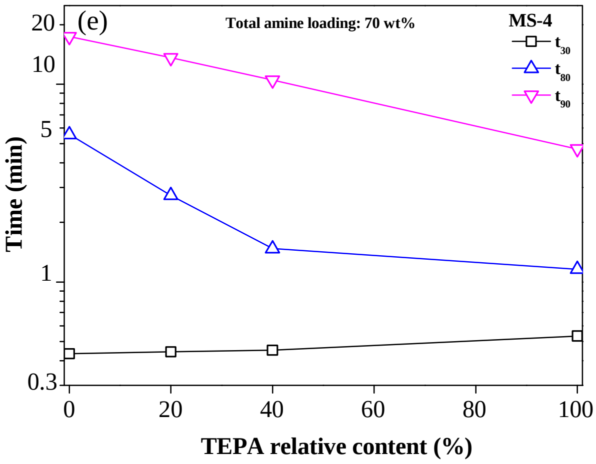


Figure 6 CO_2 adsorption kinetics of MCF-supported binary amine sorbents at 70 °C and 15% CO_2 in N_2
(a, b): Times to achieve 80% and 90% of equilibrium adsorption capacity; (c, d): effect of pore size of the silica supports on t_{80} (c) and t_{90} (d) of the supported binary amine sorbents. (e): variation of t_{30} with the relative content of TEPA in comparison with t_{80} and t_{90}

Figure 6 shows the CO_2 adsorption kinetics of the binary amine modified MCF adsorbents. The times to achieve 80 and 90% of equilibrium CO_2 adsorption capacity (t_{80} and t_{90}) were used to characterise the CO_2 adsorption kinetics of the amine sorbent materials prepared. As can be see, all the TEPA-blended PEI sorbents exhibited faster CO_2 adsorption than the mono-component PEI sorbent system and the improvement in adsorption kinetics increased with increasing levels of TEPA co-impregnation, as shown by the decrease both in t_{90} and in t_{80} in particular. For instance, as shown in Fig. 6d, compared to the t_{80} of the supported PEI (2.80 min), the time to achieve 80% of equilibrium capacity was shortened to just 1.12 min for the MS-1-supported PEI with 20 % TEPA (PEI/TEPA at 4:1 by mass) and to 1.19 min when the TEPA content was increased to 40 % (PEI/TEPA at 3:2), which were both close to the shortest t_{80} of 1.02 min obtained for the supported TEPA. This represents more than 50% reduction in the time required to reach 80% of equilibrium capacity for the binary amine sorbents, compared to the PEI sorbents at the same level of amine loading (t_{80} = 2.80 min). The largest improvement in adsorption kinetics, however, was obtained for the MS-4 supported PEI/40 wt% TEPA mixture where the time to achieve 80% of equilibrium capacity decreased by ca. 70% to just 1.47 min, compared to the 4.44 min obtained for the MS-4 supported PEI at the same amine loading of 70 wt% (4.44 min). Similarly, the t_{90} of all the supported binary amine sorbents was also found to decrease greatly with increasing relative TEPA content (Fig. 6b), though decrease was not as much as that observed for t_{80} (Fig. 6a). For example, the t_{90} was reduced by 35% for the MS-1 supported PEI/TEPA (3:2) (9.05 min) and 37% for the MS-3 supported PEI-TEPA (4:1), compared to their corresponding PEI counterparts.

Figure 6(c, d) shows the variation of t_{80} and t_{90} with the pore size of the MCF supports. For all the amine sorbents prepared, the t_{80} and t_{90} were both found to increase linearly with increase in the pore size of the MCF silica supports, indicating the increasingly faster CO_2 adsorption or reduced migration or diffusion resistance within the supported amines, due to the increased thickness of the supported amine layer as a result of the decreased surface area with increasing pore size of the support. However, it is important to note that both the t_{80} and t_{90} and their rate of increase with pore size were found to be much lower for the binary amine mixtures than for the PEI across the whole range of pore sizes examined. This suggests that the blending of TEPA into the polymeric PEI during impregnation dramatically increased the accessibility or reduced the mass transfer resistance of the supported PEI for CO_2 adsorption, particularly for the silica supports with larger pore sizes where the layer of supported PEI tends to be thicker due to their reduced surface areas. Previous studies have demonstrated that micro-cavities of varying sizes can be formed at varying scales within the impregnated bulk phase of PEI layers, leading to the decreased diffusion resistance for CO_2 migration whereas the formation of micro-cavities is less significant for impregnated low molecular mass amines [29, 32]. Compared to the impregnated mono-component PEI sorbent system, the faster adsorption rates (Fig. 6(a,b)) and higher CO_2 capacities (Fig. 5) obtained for the binary PEI/TEPA sorbents suggest that the co-impregnation of TEPA with the polymeric PEI appears to be able to significantly enhance the formation of micro-cavities within the bulk phase of the supported amine layers, because of the reduced viscosity and hence increased thermal mobility of the supported amine layer.

Fig. 6e shows the times to achieve 30% of equilibrium capacity (t_{30}) in comparison with t_{80} and t_{90} for the amine sorbent materials. Surprisingly, it was found that the PEI had a considerably shorter t_{30} than TEPA whilst the t_{30} of the binary PEI-TEPA sorbents increased with increasing content of TEPA, being in contrast to the trends observed for the t_{80} and t_{90}. This means that both the PEI and its binary blends with TEPA all achieved faster adsorption kinetics than the TEPA sorbent during the early stages of CO_2 adsorption, despite their intrinsically lower abundances of primary and secondary amino-functional groups as shown by the FTIR spectra in Fig. S1for the TEPA, PEI and binary amine modified adsorbents. This highlights the higher initial accessibility of the amine functional groups or lower mass transfer resistance of CO_2 in both the PEI and its blends with TEPA, indicating the presence of higher levels of micro-cavities and channels for CO_2 diffusion in the silica-supported PEI and PEI/TEPA than in the

TEPA sorbents. However, it appears that the size of the micro-cavities decreased slightly with increasing content of TEPA in the binary sorbents as indicated by the increased t_{30} (Fig. 6e), presumably due to the enhanced formation of smaller micro-cavities as a result of the co-impregnation, giving rise to increased mass transfer resistance during early stages of adsorption. Nevertheless, the formation of smaller micro-cavities or channels appeared to lead to increased adsorption capacity with faster adsorption kinetics during later stages of CO_2 adsorption, as shown in Fig. 5(a,b) and Fig. 6(a,b), due to the increased exposure or dispersion of the amines at finer scales and as the adsorption became less diffusion-controlled after early stages of adsorption.

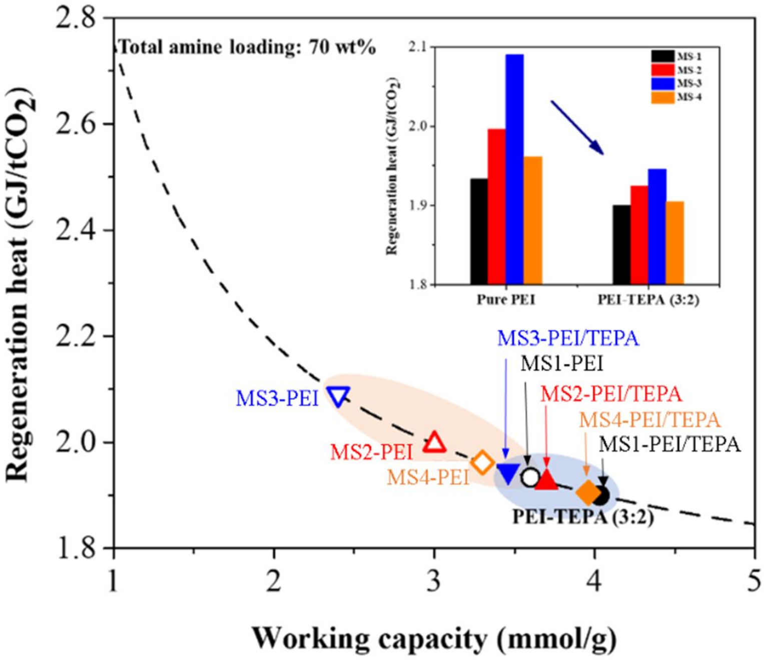


Figure 7 the relationship between regeneration energy and working capacity

The regeneration heat of adsorbent is critical in determining the CO_2 capture cost and therefore has been considered as the most important criteria to evaluate the economic performance of a commercial scale CO_2 capture plant. Our results demonstrate that the blending of TEPA as a substitute for CO_2-inactive surfactants or dispersants can greatly improve the overall performance of PEI-based adsorbent materials for CO_2 capture in terms of both the adsorption capacity and adsorption kinetics, leading to increased process efficiency and reduced energy penalty according to previous investigations [53, 82]. Based on a temperature-swing adsorption process with circulating fluidised bed technology for CO_2 capture [83] and using the methodologies reported previously (Supplementary material), the energy requirement of sorbent regeneration, which represents the major part of the energy penalty of CO_2 capture, was assessed for the TEPA-blended PEI sorbent materials in comparison with the mono-component PEI sorbent system, and the results are shown in Figure 7. It can be found that the regeneration energy requirement decreased greatly with increase in the adsorption capacity. Depending on the content of the PEI impregnated, the regeneration energy of the MCF-supported mono-component PEI adsorbents varied from 1.93 to 2.09 GJ/t CO_2, which is approximately only half of the energy requirement of a typical MEA system (3.9 GJ/tCO_2) [53]. Compared to the PEI adsorbents, a further up to 10% decrease in regeneration energy requirement could be obtained for the TEPA-blended PEI adsorbent materials, due to the improvements in both the adsorption capacity and adsorption kinetics, which together led to higher working capacities.

3.2.3 Cyclic performance testing of amine-modified MCF adsorbents

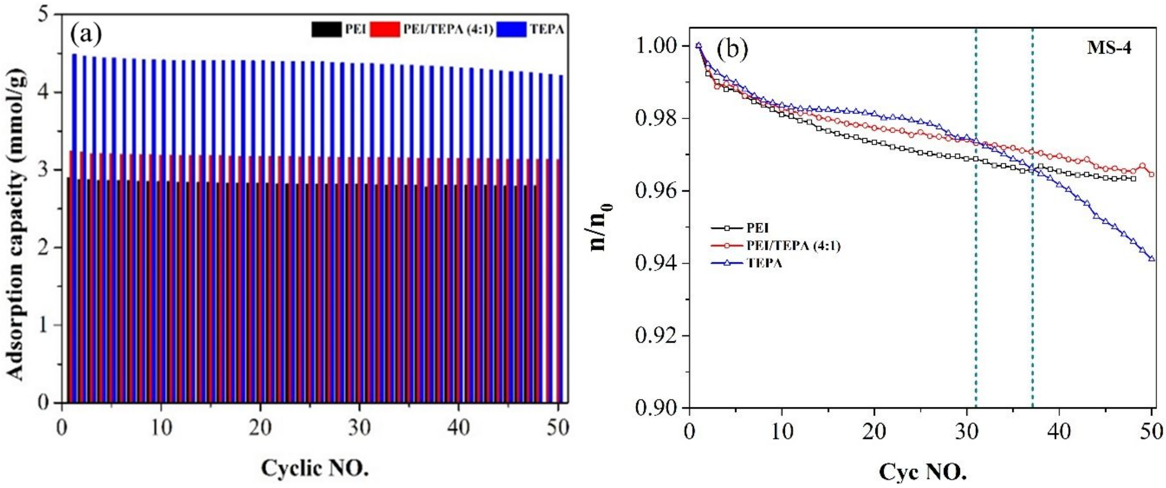


Figure 8 Cyclic adsorption–desorption profiles of selected amine modified MCF adsorbents at70 wt% amine loading in simulated flue gas with a CO_2 partial pressure of 15% CO_2 in N_2. (a): cyclic adsorption-desorption profiles in TGA conditions; (b): variation of normalized adsorption capacities with adsorption-desorption cycles; adsorption temperature: 70 °C; desorption temperature: 100 °C.

In practical applications, in addition to high CO_2 adsorption capacity, the regenerability and cyclic stability of CO_2 adsorbents, which determines their life-time performance, are also of vital importance. Therefore, which showed the best performance were selected for cyclic adsorption-desorption tests under simulated flue gas condition by temperature swing process. Figure 8 shows the cyclic adsorption-desorption performance for the selected best-performing PEI, TEPA and binary amine adsorbent materials. It can be found that during the 50 cycles of adsorption-desorption tests, both the PEI and the PEI-TEPA binary amine adsorbents exhibited significantly higher cyclic stability than the mono-component TEPA sorbent system, which showed a steady decrease with increase in the number of adsorption-desorption cycles. To better reveal the cyclic performance of the sorbents for CO_2 adsorption, Fig. 8b shows the variation of normalized CO_2 adsorption capacities with the number of adsorption cycles. The normalised CO_2 capacity was defined as the ratio between the cyclic CO_2 capacity (C_n) achieved by an adsorbent material in a specific cycle to the initial CO_2 capacity (C_0) of the adsorbent. As shown in Fig. 8b, the PEI-TEPA binary amine sorbent surprisingly exhibited higher as opposed to lower thermal stability or cyclic performance than the supported PEI sorbent, despite the higher thermal volatility of the TEPA co-impregnated. The CO_2 capacity of the PEI-TEPA sorbent decreased slightly by a total of only 3.4% from 3.24 to 3.13 mmol/g over the 50 cycles test, being lower the 3.8% loss observed for the PEI sorbent (from 2.90 to 2.79 mmol/g). As expected, the mono-component TEPA sorbent appeared to be the least stable, where the losses in CO_2 capacity were found to accelerate significantly with increasing number of adsorption cycles particularly after the first 30 cycles of the test, as shown in Fig.8b. It is generally believed that the loss in CO_2 capacity of amine-based sorbent systems arises from the evaporation loss of impregnated amines typically due to the presence of lower boiling amine components present as impurities in the amine for impregnation [29] and from the thermal and/or oxidative degradation of the amines over time [84]. The small but sharp losses in CO_2 capacity observed in the first few cycles for all the amine sorbents prepared were clearly because of the evaporation loss of the lower boiling amine impurities present in the PEI and TEPA for impregnation, whereas the losses in CO_2 capacity in following cycles were attributable mainly to the irreversible urea formation particularly at the higher temperatures used for desorption. In addition, the cyclic adsorption-desorption performance for selected adsorbents in extreme case using pure CO_2 as stripping gas was also carried out. As shown in Figure S2, similar to the results obtained by using nitrogen as stripping gas, both the PEI and the PEI-TEPA binary amine adsorbents exhibited significantly higher stability than the TEPA sorbent system during the 50 cycles of adsorption-desorption tests. However, due to extreme desorption condition used, the adsorption capacity obtained was relatively low. In reality, steam or steam-CO_2 mixture in place of pure CO_2 was practically used in regeneration process, much higher adsorption capacity can be achieved [85]. Though further investigations may be needed, the much lower losses observed for the binary PEI-TEPA than for the TEPA sorbent suggest that the co-impregnation of PEI and TEPA greatly suppressed the urea formation, presumably due to the induced dilution of primary amine functionalities, which are most liable to urea formation [84, 86], and the formation of micro-cavities at finer scales that can effectively reduce the resistance of CO_2 diffusion into and out of the supported binary amine layers during the adsorption and high temperature desorption cycles [32].

4 Conclusions

A range of three-dimensional porous silica materials with interconnected pore structures have been synthesised and used to prepare supported binary PEI-TEPA adsorbent materials for CO_2 capture in comparison with the mono-component PEI and TEPA sorbent systems. While all the prepared materials exhibited high performance for CO_2 adsorption, the binary PEI-TEPA sorbents showed the best performance, as highly characterised by the dramatically increased CO_2 capacity and adsorption kinetics compared to the mono-component PEI and TEPA sorbent systems. The characterisations demonstrate that the CO_2 adsorption capacity and adsorption kinetics both increased with increase in the relative content of TEPA in the binary sorbent system. At a total amine loading level of 70 wt%, the CO_2 capacity of the best-performing PEI sorbent with 40 wt% TEPA co-impregnated were found to be 45% higher than those of the mono-component PEI sorbent system, while the times to achieve 80 and 90% of equilibrium capacity was decreased by 70% and 35%, respectively. However, the co-impregnation of PEI and TEPA was found to lead to decreased adsorption kinetics at the initial stages of CO_2 adsorption, though the decrease was insignificant. Cyclic adsorption-desorption tests confirm that all binary PEI-TEPA sorbents exhibited higher cyclic stability particularly if compared to the mono-component TEPA sorbent systems. The cyclic testing results also tend to suggest that the co-impregnation can greatly suppress irreversible urea formation during CO_2 adsorption and desorption cycles, presumably due to the induced dilution of primary amine functionalities and enhanced formation of micro-cavities at finer scales within the supported binary amine layers.

Acknowledgement

We thank Dr. Martin Roe and Dr Elisabeth Steer for their kind assistance with SEM measurements.

References

[1] Haszeldine RS. Carbon capture and storage: how green can black be? Science 2009; 325: 1647–1652.

[2] The Committee on Climate Change. Net Zero: The UK's contribution to stopping global warming, https://www.theccc.org.uk/wp-content/uploads/2019/05/Net-Zero-The-UKs-contribution-to-stopping-global-warming.pdf; 2019 [accessed 24 May 2019].

[3] Boot-Handford ME, Abanades JC, Anthony EJ, Blunt MJ, Brandani S, Mac Dowell N, Fernández JR, Ferrari MC, Gross R, Hallett JP, Haszeldine RS. Carbon capture and storage update. Energy Environ. Sci. 2014; 7(1) 130-189.

[4] Rochelle GT. Amine scrubbing for CO_2 capture. Science 2009; 325: 1652–1654.

[5] Nguyen T, Hilliard M, Rochelle GT. Amine volatility in CO_2 capture. Int. J. Greenh. Gas. Control 2010; 4: 707–715.

[6] Oschatz M, Antonietti M. A search for selectivity to enable CO_2 capture with porous adsorbents. Energy Environ. Sci. 2018; 11(1): 57-70.

[7] Lee, A.S., Eslick, J.C., Miller, D.C., Kitchin, J.R., 2013. Comparisons of amine solvents for post-combustion CO_2 capture: A multi-objective analysis approach. Int. J. Greenh. Gas Con. 18, 68-74.

[8] Vitillo, J.G., Smit, B., Gagliardi, L., 2017. Introduction: carbon capture and separation. Chem. Rev. 117, 9521−9523.

[9] Lin LC, Berger AH, Martin RL, Kim J, Swisher JA, Jariwala K, Rycroft CH, Bhown AS, Deem MW, Haranczyk M, Smit B. In silico screening of carbon-capture materials. Nature Mater. 2012; 11: 633–641.

[10] The Mission Innovation Carbon Capture, Utilization, and Storage (CCUS) Expert's Workshop. Accelerating Breakthrough Innovation in Carbon Capture, Utilization, and Storage. https://www.energy.gov/fe/downloads/accelerating-breakthrough-innovation-carbon-capture-utilization-and-storage, 2017 [accessed 15 July 2019].

[11] Bollini P, Didas SA, Jones CW. Amine-oxide hybrid materials for acid gas separations. J. Mater. Chem. 2011; 21(39): 15100-15120.

[12] Bae TH, Hudson MR, Mason JA, Queen WL, Dutton JJ, Sumida K, Micklash KJ, Kaye SS, Brown CM, Long JR. Evaluation of cation-exchanged zeolite adsorbents for post-combustion carbon dioxide capture. Energy Environ. Sci. 2013; 6: 128-138.

[13] Zhang Z, Yao ZZ, Xiang S, Chen B. Perspective of microporous metal–organic frameworks for CO_2 capture and separation. Energy Environ. Sci. 2014; **7**: 2868–2899.

[14] Liu J, Sun N, Sun C, Liu H, Snape C, Li K, Wei W, Sun Y. Spherical potassium intercalated activated carbon beads for pulverised fuel CO2 post-combustion capture. Carbon 2015; 94:243-255.

[15] Liu X, Sun Y, Liu J, Sun C, Liu H, Xue Q, Smith E, Snape C. Potassium and zeolitic structure modified ultra-microporous adsorbent materials from a renewable feedstock with favorable surface chemistry for CO_2 capture. ACS Appl. Mater. Interfaces 2017; 9(32): 26826-26839.

[16] Liu X, Sun C, Liu H, Tan WH, Wang W, Snape C. Developing hierarchically ultra-micro/mesoporous biocarbons for highly selective carbon dioxide adsorption. Chem. Eng. J. 2019; 361: 199-208.

[17] Gray, M.L., Champagne, K.J., Fauth, D., Baltrus, J.P., Pennline, H., 2008. Performance of immobilized tertiary amine solid sorbents for the capture of carbon dioxide. Int. J. Greenh. Gas Con. 2(1), 3-8.

[18] Hicks JC, Drese JH, Fauth DJ, Gray ML, Qi G, Jones CW. Designing adsorbents for CO_2 capture from flue gas-hyperbranched aminosilicas capable of capturing CO_2 reversibly. J. Am. Chem. Soc. 2008; 130(10): 2902-2903.

[19] Czaun M, Goeppert A, May RB, Peltier D, Zhang H, Prakash GS, Olah GA. Organoamines-grafted on nano-sized silica for carbon dioxide capture. J. CO_2 Util. 2013; 1: 1-7.

[20] Dutcher B, Fan M, Russell AG. Amine-based CO_2 capture technology development from the beginning of 2013-A Review. ACS Appl. Mater. Interfaces 2015; 7(4): 2137-2148.

[21] Lashaki MJ, Sayari A. CO_2 capture using triamine-grafted SBA-15: The impact of the support pore structure. Chem. Eng. J. 2018; 334: 1260-1269.

[22] Linneen NN, Pfeffer R, Lin YS. CO_2 adsorption performance for amine grafted particulate silica aerogels. Chem. Eng. J. 2014; 254: 190-197.

[23] Kishor R, Ghoshal AK. APTES grafted ordered mesoporous silica KIT-6 for CO_2 adsorption. Chem. Eng. J. 2015; 262: 882-890.

[24] Ma X, Wang X, Song C. "Molecular basket" sorbents for separation of CO_2 and H_2S from various gas streams. J. Am. Chem. Soc. 2009; 131(16): 5777-5783.

[25] Zhang H, Goeppert A, Kar S, Prakash GS. Structural parameters to consider in selecting silica supports for polyethylenimine based CO_2 solid adsorbents: Importance of pore size. J. CO_2 Util. 2018; 26: 246-253.

[26] Panek R, Wdowin M, Franus W, Czarna D, Stevens LA, Deng H, Liu J, Sun C, Liu H, Snape CE. Fly ash-derived MCM-41 as a low-cost silica support for polyethyleneimine in post-combustion CO_2 capture. J. CO_2 Util. 2017; 22: 81-90.

[27] Meng Y, Jiang J, Gao Y, Yan F, Liu N, Aihemaiti A. Comprehensive study of CO_2 capture performance under a wide temperature range using polyethyleneimine-modified adsorbents. J. CO_2 Util. 2018; 27: 89-98.

[28] Zhang H, Goeppert A, Olah GA, Prakash GS. Remarkable effect of moisture on the CO_2 adsorption of nano-silica supported linear and branched polyethylenimine. J. CO_2 Util. 2017; 19: 91-99.

[29] Sun Y, Liu X, Sun C, Al-Sarraf W, Foo KZ, Meng Y, Lee S, Wang W, Liu H. Synthesis and functionalisation of spherical meso-, hybrid meso/macro-and macro-porous cellular silica foam materials with regulated pore sizes for CO_2 capture. J. Mater. Chem. A 2018; 6(46): 23587-23601.

[30] Goeppert A, Meth S, Prakash GS, Olah GA. Nanostructured silica as a support for regenerable high-capacity organoamine-based CO_2 sorbents. Energy Environ. Sci. 2012; 3: 1949–1960.

[31] Wang X, Chen L, Guo Q. Development of hybrid amine-functionalized MCM-41 sorbents for CO_2 capture. Chem. Eng. J. 2015; 260: 573-581.

[32] Builes S, Vega LF. Effect of immobilized amines on the sorption properties of solid materials: impregnation versus grafting. Langmuir 2012; 29(1): 199-206.

[33] Franchi RS, Harlick PJ, Sayari A. Applications of pore-expanded mesoporous silica. 2. Development of a high-capacity, water-tolerant adsorbent for CO_2. Ind. Eng. Chem. Res 2005; 44(21): 8007-8013.

[34] Alkhabbaz MA, Khunsupat R, Jones CW. Guanidinylated poly (allylamine) supported on mesoporous silica for CO_2 capture from flue gas. Fuel 2014; 121: 79-85.

[35] Zeng W, Bai H. Swelling-agent-free synthesis of rice husk derived silica materials with large mesopores for efficient CO_2 capture. Chem. Eng. J. 2014; 251: 1-9.

[36] Feng X, Hu G, Hu X, Xie G, Xie Y, Lu J, Luo M. Tetraethylenepentamine-modified siliceous mesocellular foam (MCF) for CO_2 capture. Ind. Eng. Chem. Res 2013; 52(11): 4221-4228.

[37] Kishor R, Ghoshal, AK. High molecular weight polyethyleneimine functionalized three-dimensional mesoporous silica for regenerable CO_2 separation. Chem. Eng. J. 2016; 300: 236-244.

[38] Mello MR, Phanon D, Silveira GQ, Llewellyn PL, Ronconi CM. Amine-modified MCM-41 mesoporous silica for carbon dioxide capture. Micropor. Mesopor. Mat. 2011; 143(1): 174-179.

[39] Kim S, Ida J, Guliants VV, Lin YS. Tailoring pore properties of MCM-48 silica for selective adsorption of CO_2. J. Phys. Chem. B 2005; 109(13): 6287-6293.

[40] Chen C, Son WJ, You KS, Ahn JW, Ahn WS. Carbon dioxide capture using amine-impregnated HMS having textural mesoporosity. Chem. Eng. J. 161(1-2) (2010) 46-52.

[41] Son WJ, Choi JS, Ahn WS. Adsorptive removal of carbon dioxide using polyethyleneimine-loaded mesoporous silica materials. Micropor. Mesopor. Mat. 2008; 113(1-3): 31-40.

[42] Subagyono DJ, Liang Z, Knowles GP, Chaffee AL. Amine modified mesocellular siliceous foam (MCF) as a sorbent for CO_2. Chem. Eng. Res. Des. 2011; 89(9): 1647-1657.

[43] Zhang W, Liu H, Sun C, Drage TC, Snape CE. Performance of polyethyleneimine–silica adsorbent for post-combustion CO_2 capture in a bubbling fluidized bed. Chem. Eng. J. 2014; 251: 293-303.

[44] Pino L, Italiano C, Vita A, Fabiano C, Recupero V. Recupero, Sorbents with high efficiency for CO_2 capture based on amines-supported carbon for biogas upgrading. J. Environ. Sci. 2016; 48: 138-150.

[45] Sanz-Pérez ES, Olivares-Marín M, Arencibia A, Sanz R, Calleja G, Maroto-Valer MM. CO_2 adsorption performance of amino-functionalized SBA-15 under post-combustion conditions. Int. J. Greenh. Gas. Control 2013; 17: 366-375.

[46] Li K, Jiang J, Tian S, Yan F, Chen X. Polyethyleneimine–nano silica composites: a low-cost and promising adsorbent for CO_2 capture. J. Mater. Chem. A 2015; 3(5): 2166-2175.

[47] Chen C, Yang ST, Ahn WS, Ryoo R. Amine-impregnated silica monolith with a hierarchical pore structure: enhancement of CO_2 capture capacity. Chem. Commun. 2009; 24: 3627–3629.

[48] Zhang W, Liu H, Sun C, Drage TC, Snape CE. Capturing CO_2 from ambient air using a polyethyleneimine–silica adsorbent in fluidized beds. Chem. Eng. Sci. 2014; 116:306-316.

[49] Li K, Jiang J, Yan F, Tian S, Chen X. The influence of polyethyleneimine type and molecular weight on the CO_2 capture performance of PEI-nano silica adsorbents. Appl. Energy 2014; 136:750-755.

[50] Gray ML, Hoffman JS, Hreha DC, Fauth DJ, Hedges SW, Champagne KJ, Pennline HW. Parametric study of solid amine sorbents for the capture of carbon dioxide. Energy Fuels 2009; 23(10):4840-4844.

[51] Sjostrom S, Krutka H. Evaluation of solid sorbents as a retrofit technology for CO_2 capture. Fuel 2010; 89(6):1298-1306.

[52] Quang DV, Dindi A, Rayer AV, Hadri NE, Abdulkadir A, Abu-Zahra MR. Effect of moisture on the heat capacity and the regeneration heat required for CO_2 capture process using PEI impregnated mesoporous precipitated silica. Greenh. Gases 2015; 5(1): 91-101.

[53] Zhang W, Liu H, Sun Y, Cakstins J, Sun C, Snape CE. Parametric study on the regeneration heat requirement of an amine-based solid adsorbent process for post-combustion carbon capture. Appl. Energy 2016; 168:394-405.

[54] Satyapal S, Filburn T, Trela J, Strange J. Performance and properties of a solid amine sorbent for carbon dioxide removal in space life support applications. Energy Fuels 2001; 15(2): 250-255.

[55] Xu X, Song C, Andresen JM, Miller BG, Scaroni AW. Preparation and characterization of novel CO_2 "molecular basket" adsorbents based on polymer-modified mesoporous molecular sieve MCM-41. Micropor. Mesopor. Mat. 2003; 62: 29-45.

[56] Meth S, Goeppert A, Prakash GS, Olah GA. Silica nanoparticles as supports for regenerable CO_2 sorbents. Energy Fuels 2012; *26*(5): 3082-3090.

[57] Sakwa-Novak MA, Tan S, Jones CW. Role of additives in composite PEI/Oxide CO_2 adsorbents: enhancement in the amine efficiency of supported PEI by PEG in CO_2 capture from simulated ambient air. ACS Appl. Mater. Interfaces 2015; 7(44): 24748-24759.

[58] Wang J, Long D, Zhou H, Chen Q, Liu X, Ling L. Surfactant promoted solid amine sorbents for CO_2 capture. Energy Environ. Sci. 2012; 5(2): 5742-5749.

[59] Tanthana J, Chuang SS. In Situ Infrared Study of the Role of PEG in Stabilizing Silica-Supported Amines for CO_2 Capture. ChemSusChem 2010; *3*(8): 957-964.

[60] Starkie CM, Amieiro-Fonseca A, Rigby SP, Drage TC, Lester EH. Surfactant mediated CO_2 adsorption: the role of the co-impregnation species. Energy Procedia 2014; 63: 2323-2330.

[61] Heydari-Gorji A, Belmabkhout Y, Sayari A. Polyethylenimine-impregnated mesoporous silica: effect of amine loading and surface alkyl chains on CO_2 adsorption. Langmuir 2011; 27(20): 12411-12416.

[62] Dao DS, Yamada H, Yogo K. Large-pore mesostructured silica impregnated with blended amines for CO_2 capture. Ind. Eng. Chem. Res. 2013; 52(38): 13810-13817.

[63] Yue MB, Sun LB, Cao Y, Wang ZJ, Wang Y, Yu Q, Zhu JH. Promoting the CO2 adsorption in the amine-containing SBA-15 by hydroxyl group. Micropor. Mesopor. Mat. 2008;114(1-3):74-81.

[64] Sanz R, Calleja G, Arencibia A, Sanz-Pérez ES. Development of high efficiency adsorbents for CO_2 capture based on a double-functionalization method of grafting and impregnation. J. Mater. Chem. A 2013;1(6):1956-1962.

[65] Sánchez-Zambrano K, Lima Duarte L, Soares Maia D, Vilarrasa-García E, Bastos-Neto M, Rodríguez-Castellón E, Silva de Azevedo D. CO2 capture with mesoporous silicas modified with amines by double functionalization: Assessment of adsorption/desorption cycles. Materials 2018;11(6):887.

[66] Fauth DJ, Gray ML, Pennline HW, Krutka HM, Sjostrom S, Ault AM. Investigation of porous silica supported mixed-amine sorbents for post-combustion CO2 capture. Energy Fuels 2012;26(4):2483-2496.

[67] Schmidt-Winkel P, Lukens WW, Yang P, Margolese DI, Lettow JS, Ying JY, Stucky GD. Microemulsion templating of siliceous mesostructured cellular foams with well-defined ultralarge mesopores. Chem. Mater. 2000; 12(3): 686-696.

[68] Sing, KS. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. Pure Appl. Chem. 1985; 57(4): 603-619.

[69] Lukens WW, Schmidt-Winkel P, Zhao D, Feng J, Stucky GD. Evaluating pore sizes in mesoporous materials: A simplified standard adsorption method and a simplified Broekhoff-de Boer method. Langmuir 1999; 15(16): 5403-5409.

[70] Yan X, Zhang L, Zhang Y, Qiao K, Yan Z, Komarneni S. Amine-modified mesocellular silica foams for CO_2 capture. Chem. Eng. J. 2011; 168(2): 918-924.

[71] Wang X, Guo Q, Zhao J, Chen L. Mixed amine-modified MCM-41 sorbents for CO_2 capture. Int. J. Greenh. Gas. Control 2015; 37: 90-98.

[72] Yan X, Zhang L, Zhang Y, Yang G, Yan Z. Amine-modified SBA-15: effect of pore structure on the performance for CO_2 capture. Ind. Eng. Chem. Res 2011; 50(6): 3220-3226.

[73] Liu Y, Yu X. Carbon dioxide adsorption properties and adsorption/desorption kinetics of amine-functionalized KIT-6. Appl. Energy 2018; 211: 1080-1088.

[74] Yue MB, Chun Y, Cao Y, Dong X, Zhu JH. CO_2 capture by as- prepared SBA- 15 with an occluded organic template. Adv. Fun. Mater. 2006; 16(13): 1717-1722.

[75] Liu SH, Wu CH, Lee HK, Liu SB. Highly stable amine-modified mesoporous silica materials for efficient CO_2 capture. Top. Cata. 2010; 53(3-4): 210-217.

[76] Veneman R, Li ZS, Hogendoorn JA, Kersten SR, Brilman DW. Brilman, Continuous CO_2 capture in a circulating fluidized bed using supported amine sorbents. Chem. Eng. J. 2012; 207: 18-26.

[77] Al-Marri MJ, Khader MM, Tawfik M, Qi G, Giannelis EP. Giannelis, CO_2 sorption kinetics of scaled-up polyethylenimine-functionalized mesoporous silica sorbent. Langmuir 2015; 31(12): 3569-3576.

[78] Choi S, Drese JH, Jones CW. Adsorbent materials for carbon dioxide capture from large anthropogenic point sources. ChemSusChem 2009; 2(9): 796-854.

[79] Qi G, Wang Y, Estevez L, Duan X, Anako N, Park AH, Li W, Jones CW, Giannelis EP. High efficiency nanocomposite sorbents for CO_2 capture based on amine-functionalized mesoporous capsules. Energy Environ. Sci. 2011; 4(2): 444-452.

[80] Gutowski KE, Maginn EJ. Amine-functionalized task-specific ionic liquids: a mechanistic explanation for the dramatic increase in viscosity upon complexation with CO_2 from molecular simulation. J. Am. Chem. Soc. 2008; 130(44): 14690-14704.

[81] Zhao J, Simeon F, Wang Y, Luo G, Hatton TA. Polyethylenimine-impregnated Siliceous Mesocellular Foam Particles as High Capacity CO_2 Adsorbents. RSC Adv. 2012; 2: 6509-6519.

[82] Martín CF, Sweatman MB, Brandani S, Fan X. Wet impregnation of a commercial low cost silica using DETA for a fast post-combustion CO_2 capture process. Appl. Energy 2016; 183:1705-1721.

[83] Zhang, W, Sun, C, Snape, CE, Irons, R, Stebbing, S, Alderson, T, Fitzgerald, D, Liu, H. Process simulations of post-combustion CO_2 capture for coal and natural gas-fired power plants using a polyethyleneimine/silica adsorbent. Int. J. Greenh. Gas. Control. 2017; 58: 276-289.

[84] Sayari, A. and Belmabkhout, Y. Stabilization of amine-containing CO_2 adsorbents: dramatic effect of water vapor. J. Am. Chem. Soc. 2010; 132: 6312-6314.

[85] Li W, Choi S, Drese JH, Hornbostel M, Krishnan G, Eisenberger PM, Jones CW. Steam-stripping for regeneration of supported amine- based CO2 adsorbents. ChemSusChem 2010; 23;3(8):899-903.

[86] Choi W, Min K, Kim C, Ko YS, Jeon JW, Seo H, Park YK, Choi M. Epoxide-functionalization of polyethyleneimine for synthesis of stable carbon dioxide adsorbent in temperature swing adsorption. Nat. Commun. 2016; 30:12640.