

# CO<sub>2</sub> capture adsorbents functionalized by amine – bearing polymers: A review

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## ABSTRACT

Efforts to capture CO<sub>2</sub> from anthropogenic sources as well as from the air are being continuously intensified as to battle the greenhouse gas effects and climate change. Capture by liquid solvent absorption, mainly involving amines, is the common industrial practice, yet capture relying on solid adsorbents is increasingly gaining interest due to its potential for less energy-demanding and more efficient operation. Despite the large variety of porous adsorbents being explored, such as zeolites, carbons, mesoporous silicas, graphene and related structures, polymers, and metal-organic frameworks, it still remains challenging to find a proper material to cover all the critical specifications, i.e. with respect to CO<sub>2</sub> capacity, selectivity, chemical and thermal stability, fast kinetics, cyclability, low energy consumption, low manufacturing cost, and mechanical robustness. To this end, combining highly CO<sub>2</sub>-philic amines with the most robust of the developed solid porous materials through functionalization of the latter is a highly promising approach. Consequently, particular emphasis is given to increase the number of amine functional groups per unit of support area, enhance CO<sub>2</sub>-philicity of the amines, and provide suitable diffusion pathways to enhance CO<sub>2</sub> capacity. Towards achieving this goal, use of amine-bearing polymer functionalities is being highly investigated. This work critically and comparably reviews current progress on polymeric amine - functionalized solid adsorbents and their performance in CO<sub>2</sub> capture. It examines works based on various polymers, including polyethylenimine, polypropylenimine, polyallylamine, polyaniline, amino dendrimers, and hyperbranched polyamines. Based on the extracted comparisons, optimal systems are proposed and envisioned and future trends and directions are stated.

## 1. Introduction

Because of the increasing environmental impact related to climate change and global warming, which is mainly the result of the escalating fossil fuel consumption and associated combustion products emission, research community has put immense attention in limiting the release of the carbon dioxide, as the main greenhouse gas (GHG) contributor, to the atmosphere (Alivisatos and Buchanan, 2010; Bae and Snurr, 2011; Darunte et al., 2016; Iqbal et al., 2017; Kontos et al., 2014; Lee and Park, 2015; Tabish et al., 2020; Varghese and Mittal, 2018; Varghese et al., 2020). The affect can be limited by either applying highly-efficient capturing and storage techniques or introducing more environment-friendly (green) energy resources (Olivares-Marín and Maroto-Valer, 2012; Wang et al., 2011). Among the major combustion flue gas constituents, namely CO<sub>2</sub>, SO<sub>2</sub>, N<sub>2</sub>O, N<sub>2</sub>, and unburned fuel, CO<sub>2</sub> is observed to be abundantly present in the atmosphere in continuously

increasing concentrations that currently exceed the 400 ppm level (Dillon et al., 2015; Varghese and Mittal, 2018; Varghese et al., 2020). In addition to fuel combustion, such increase in CO<sub>2</sub> concentration has also been contributed by industrial chemical processes, gas and oil treatment, as well as naturally occurring volcanic eruptions (Shen et al., 2017). Capture and sequestration currently constitute the most prominent options to reduce the atmospheric CO<sub>2</sub> accumulation and its negative effects, often offering attractive combination of performance and cost (Dzubak et al., 2012; Mikkelsen et al., 2010; Varghese et al., 2020; Yu et al., 2008). Notably, CO<sub>2</sub> capture from ambient air or direct air capture (DAC) is an emerging technology, which can achieve point-source capture through the capture from inaccessible as well as distributed sources, and address residual emissions. DAC has the potential to contribute in various ways to suppress atmospheric CO<sub>2</sub> levels, such as compensation of emissions from mobile sources, suitability at remote storage sites, re-capturing of leaked CO<sub>2</sub>, feedstock contributor for

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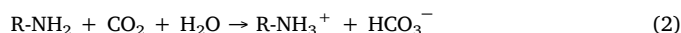
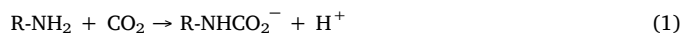
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synthetic fuel production, and help towards realization of negative emission levels (Armstrong et al., 2019; Lackner et al., 2012; Shi et al., 2019; Wijesiri et al., 2019). The immense attention for CO<sub>2</sub> capture is also related to the appearance of CO<sub>2</sub> as one of the major impurities in the shale gas (Xian et al., 2015a).

A number of studies have been reported supporting that the capture of CO<sub>2</sub> can be effectively undertaken through absorption, adsorption, membrane separation, or cryogenic distillation processes (Favvas et al., 2019; Iqbal et al., 2016; Labropoulos et al., 2015; Perdikaki et al., 2016, 2012; Rao and Rubin, 2006; Sakpal et al., 2012; Tzialla et al., 2013; Zainab et al., 2017). CO<sub>2</sub> capture by aqueous amine scrubbing is a traditional technology widely accepted by the industry owing also to its applicability in industrial processes such as syngas purification, H<sub>2</sub>S removal, and various other process schemes such as in steel industry. However, the regeneration and desorption of captured CO<sub>2</sub> from these liquid amine systems is an energy intensive process because of the high heat of sorption with the CO<sub>2</sub>, high heat capacity of water, and the associated requirement of high regeneration temperatures. This substantially high regeneration energy requirement adds significant operating cost to the CO<sub>2</sub> capture process, and leaves a considerable carbon footprint itself. In addition, drawbacks such as corrosion of equipment, limited capability for increasing amine concentration, heavily diffusion-limited process, and amine leakage to the environment often take place in these classical aqueous amine schemes. Notably, the environmental impact of CO<sub>2</sub> capture systems based on amines is crucial due to amine release, the photo-oxidation of amines in the influence of atmospheric oxidants, and the resultant generation of products, such as nitrosamines, nitramines, amides, etc. These compounds can affect health and pose environmental risks. For instance, nitrosamine is toxic at very low concentrations and it may cause carcinogenicity, mutagenicity and reproductive effects (Booth et al., 2011; Karl et al., 2011; Nielsen et al., 2012). To alleviate the above issues, intense research efforts are focusing on developing novel solvents and solvent combinations exhibiting lower volatility, better thermal stability, lower corrosive characteristic, lower degradation rate, and reduced regeneration cost.

Adsorption constitutes an attractive solution owing to minimal utilization of regeneration energy, high capture capacity and selectivity, processing convenience, cost effectiveness, and reduced environmental impact (Chaffee et al., 2007; Choi et al., 2009; Nigar et al., 2016; Pan et al., 2016; Samanta et al., 2011; Sayari et al., 2011; Varghese et al., 2020; Wang et al., 2011). Adsorption is a surface-dominated capture mechanism taking place when CO<sub>2</sub> comes into contact with a solid adsorbent material through weak physical interactions or stronger chemical bonding. The former is named physisorption or physical adsorption and mainly occurs via electrostatic or van der Waals forces, whereas the latter is called chemisorption or chemical adsorption (Bhown and Freeman, 2011; D'Alessandro et al., 2010; Srivastava and Eames, 1998; Varghese and Mittal, 2018; Yang, 2013). The captured CO<sub>2</sub> can be then desorbed in the regeneration step and become available for underground sequestration, enhanced oil recovery, utilization by conversion to fuel and chemicals, and more (Meth et al., 2012; Yu et al., 2008; Zhang et al., 2016a). One of the drawbacks of use of adsorbents is their poor performance in terms of adsorption capacity and selectivity at low partial pressure conditions (Mittal et al., 2015), which becomes more severe in the presence of moisture, where water can occupy active sites or compromise the stability of the adsorbent materials (Chaffee et al., 2007). To overcome these issues, adsorbent functionalization has been received considerable attention (Didas et al., 2015; Drage et al., 2008; Varghese et al., 2020; Zhang et al., 2014b). The introduction of various amine-containing basic moieties for instance into porous solid sorbents is found advantageous to markedly strengthen their capture capacity through interaction with CO<sub>2</sub> via chemical means leading to the formation of carbamates and bicarbonates when CO<sub>2</sub> comes into contact with amine in anhydrous and hydrous conditions, respectively, as shown below (Darunte et al., 2016; Khatri et al., 2006; Shen et al., 2017; Xian et al., 2015a).



Amine-functionalized adsorbents comprise a support, typically porous, with weakly bonded (impregnated) pre-made polymeric amines or small amine molecules or with covalently bonded (grafted) small amine molecules or *in situ* formed polymeric amines (Chaikittisilp et al., 2011b; Choi et al., 2011; Didas et al., 2015; Li et al., 2010b). Impregnated systems are developed through the rather facile impregnation into the support, i.e., by physical adsorption of amines. On the other hand, amine - grafted/covalently bonded systems are prepared through chemical tethering of amines to support surface upon synthesis (*in situ*) or post-synthesis modification. Amine impregnated CO<sub>2</sub> sorbent systems often exhibit high capture capacity, yet, shortcomings such as stability lack due to the leaching of amines over capture/regeneration cycles and limited transport of CO<sub>2</sub> to active support sites due to the diffusion hindrance pose challenges associated to these systems. In order to overcome these issues and improve performance and long-term sustainability, amine - grafted/covalently bonded CO<sub>2</sub> sorbent systems are being explored. The grafted/covalently bonded amines on these sorbents can grant stability over many regeneration cycles, whereas challenges associated to controlled grafting and optimization need to be given emphasis. Polymeric amines, i.e. polymers with amine moieties in their backbone or side chains, are receiving immense attention for design of supported amine based sorbent systems due to their higher content of amine groups (Cai et al., 2015; Darabi et al., 2016; Wu et al., 2015). Fig. 1 schematically portrays the introduction of polymeric amines into porous structures and the resulting CO<sub>2</sub> capture possibilities. Because of their ability to capture CO<sub>2</sub> effectively in dry as well as wet environments, polymeric amines containing more primary and secondary amine moieties are preferred for the design of supported amine capture applications (Bollini et al., 2011b; Choi et al., 2009). Primary amines for instance typically display higher enthalpy of adsorption, which makes them suitable for direct CO<sub>2</sub> capture in ultra-dilute ambiances (Bollini et al., 2011a; Chaikittisilp et al., 2011a; Li et al., 2010a).

Regarding the cost of polyamine-functionalized solid adsorbents, in order to link-up the targets of low-cost capture, one should target a reasonable cost of sorbent manufacturing. To this extent, a proper balance between selected amine functionalities, support selection, and preparation/functionalization procedure should be kept. Most of the supports used are relatively non expensive, e.g. silica, carbons, zeolites, and clays, as are most of the used amines, e.g. polyethylenimine (PEI). Also, the properties of the developed sorbents should be maintained after a number of adsorption-desorption cycles as to reduce the need for adsorbent replacement. Regarding operating cost, the main contributor comes from the substantially high regeneration energy required. For example, in the case of aqueous amines, the regeneration of absorbed CO<sub>2</sub> is an energy intensive process owing to the high regeneration temperature, cycle duration, and heat capacity of water, while solid supported amine sorbents have the potential to alleviate these issues. In comparison to aqueous amines, the lower heat capacity and facile regeneration of solid sorbents can contribute to reduce the energy consumption and thereby CO<sub>2</sub> capture cost. Furthermore, the corrosion issues associated with liquid amines, which elevate the need and associated cost for equipment maintenance and replacement, can be alleviated through the application of solid-supported amine sorbents owing to the fact that only solid-solid contact with equipment surface takes place in such systems.

Critical parameters such as adsorption capacity, selectivity, kinetics, regenerability, stability, mechanical robustness, cost, and energy consumption need to be considered when it comes to selecting adsorbent materials for effective CO<sub>2</sub> capture applications (D'Alessandro et al., 2010; Drage et al., 2008; Liu et al., 2012c; Samanta et al., 2011; Sayari et al., 2011). Thus far, various supported polymeric amine based CO<sub>2</sub>

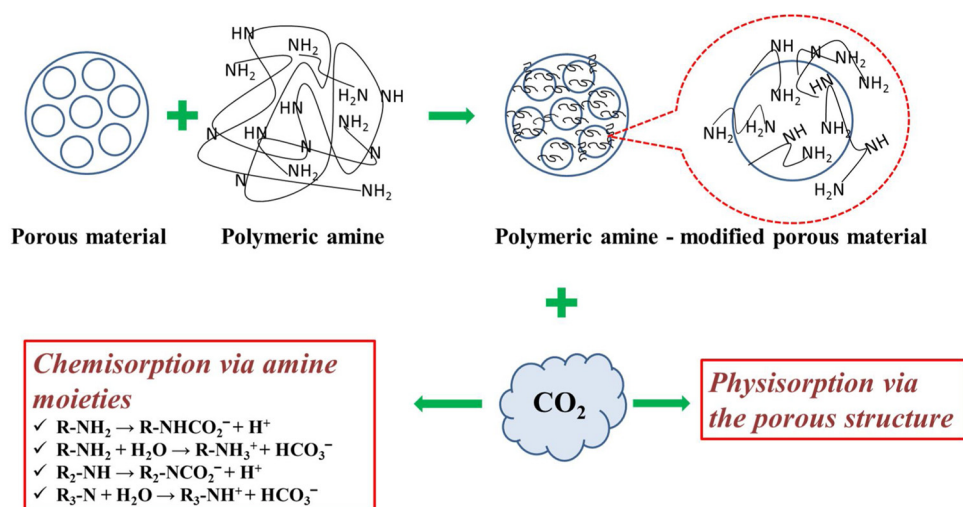


Fig. 1. Schematic of functionalization of porous materials with polymeric amines and their CO<sub>2</sub> capture action.

adsorbents have been designed through the combination of various support materials and polymeric amines. In this work, we are reviewing studies reported on polymeric amine - functionalized solid adsorbents for CO<sub>2</sub> capture, including involvement of polyethylenimine, polypropylenimine, polyallylamine, polyaniline, amino dendrimers, and hyperbranched polyamines. An overview of these polymeric amines is summarized in Table 1. For emphasizing on the technological scope, we would like to point out that the examined parameters throughout the review are tightly connected to the potential capture performance at large scale, and without such characteristics examination, successful scaled up process cannot be realized. Specifically, developments/advancements of systems based on various support materials, i.e. silica (SBA-15, MCM-41, fumed silica, precipitated silica, silica foam, silica gel, and more), different clays, graphene and related structures, carbon nanotubes, fullerene, mesoporous carbon, carbon spheres, alumina, metal-organic frameworks, zeolites, porous polymers and more, with the various polymeric amines are reviewed, compared and summarized. It is noteworthy to mention that such valuable feedback on the current status of various supported polymeric amine - based CO<sub>2</sub> sorbents is inevitable in order to effectively choose and further optimize the developed systems as to accomplish the required performance goals at the large scale process level. In this review article, the performance of the studied sorbents was compared in connection to capture capacity, selectivity, kinetics, heat of adsorption, regenerability, cyclic stability, oxidative stability, thermal stability, stability in various conditions like moisture and steam, and amine efficiency, on the basis of data availability, properties that are of critical importance for large scale implementation.

## 2. Polyethylenimine – based CO<sub>2</sub> adsorbents

Polyethylenimine, also named as polyaziridine, is one of the most highly investigated aliphatic polymeric amines for CO<sub>2</sub> sorption due to its availability, high CO<sub>2</sub> capture capability, increased amine density, primary amine chain ends, and stability as it can maintain CO<sub>2</sub> sorption capability up to 90 °C (Chaikittisilp et al., 2011b; Holeywinski et al., 2015; Subagyono et al., 2011; Xu et al., 2003). PEI grants versatility in customized functionalization as it is available in linear, branched, or dendrimer structural forms, at 300–750,000 molecular weight range (Chen et al., 2013b; Shen et al., 2017), and can contain primary, secondary, and tertiary amines at respective chain ends, back bone, and branch points (Table 1) (Chaikittisilp et al., 2011a). For CO<sub>2</sub> capture applications, the role of PEI was recognized in 2001 by Satyapal et al. (Satyapal et al., 2001) through its introduction in space applications. Thereupon, PEI is intensively investigated for various supported amine

related CO<sub>2</sub> capture applications, as reviewed in the following sections.

### 2.1. Siliceous adsorbents with PEI

By virtue of their well-ordered porous nature and pore distribution or of their amorphous nature, large specific surface area, and appreciable amine holding capability, various siliceous materials are receiving interest for designing diverse amine - supporting CO<sub>2</sub> sorbents (Cai et al., 2015; Heydari-Gorji et al., 2011a; Hoffmann et al., 2006; Meth et al., 2012; Sakpal et al., 2012), including, SBA-15, MCM-41, fumed silica, precipitated silica, mesoporous siliceous foam, and silica gel.

#### 2.1.1. SBA-15 – supported PEI

SBA-15 (SBA standing for Santa Barbara Amorphous), is an attractive mesoporous silica material having well-ordered and relatively large hexagonal pores in the range of 4.6 – 30 nm. This siliceous material was a research contribution from University of California, Santa Barbara in 1997 by Zhao et al. (Kruk et al., 2000; Zhao et al., 1998, 2000). Due to its promising features as support and CO<sub>2</sub> capture medium, a number of works have been reported that design effective SBA-15 supported PEI adsorbents, as reviewed below.

Wang et al. (Wang et al., 2013c) developed CO<sub>2</sub> adsorbents based on SBA-15 - filled with PEI with the aid of wet impregnation by varying the filling amount of linear polyethylenimine (LPEI). The mesoporous nature of SBA-15 was shown to be well preserved after the infusion of LPEI. Adsorption studies in a fixed-bed system at 75 °C and atmospheric pressure revealed that the 60 wt% LPEI ( $M_w = 423$ ) system exhibited a maximum adsorption capacity of ca. 3.51 mmol g<sup>-1</sup>. In another study, Wang et al. (Wang et al., 2012b) used 50 wt% of PEI ( $M_n = 423$ ) with SBA-15 and the observed CO<sub>2</sub> uptake values in 1% CO<sub>2</sub> were ca. 1.44 and 1.52 mmol g<sup>-1</sup> referring to breakthrough and saturation capacities at 75 °C and 1 atm. Moreover, selectivities of 14 and 185 were reported for CO<sub>2</sub>/CO and CO<sub>2</sub>/Ar mixtures, respectively. Notably, the stability remained almost unaffected up to 20 adsorption-desorption cycles. Ahmadalinezahad et al. (Ahmadalinezahad and Sayari, 2014) reported the functionalization of SBA-15 using LPEI- and branched polyethylenimine (BPEI), and also examined their behavior against oxidation-induced degradation. The LPEI - based system showed higher oxidation resistance as compared to the BPEI based one, while the products of degradation were characterized by means of nuclear magnetic resonance (NMR) of solvent-extracted deactivated species.

Gargiulo et al. (Gargiulo et al., 2014) developed PEI - functionalized SBA-15 and revealed the effectiveness of pore filling from N<sub>2</sub> adsorption-desorption at 77 K. In this study, PEI - functionalized mesoporous silica exhibited a CO<sub>2</sub> capacity of ca. 0.81 mmol g<sup>-1</sup> at 25 °C and 1 atm,

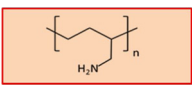
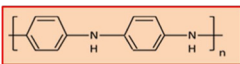
**Table 1**  
Details of polymeric amines reported for CO<sub>2</sub> capture applications.

S.No.	Polymeric amine	Chemical structure	Remarks
1.	Polyethylenimine (or polyaziridine)		Wide availability in various structural forms and molecular weights.
1.a.	Linear polyethylenimine		Secondary amines on the back bone.
1.b.	Branched polyethylenimine		Primary, secondary, and tertiary amines at respective chain ends, back bone, and branch points.
1.c.	Polyethylenimine dendrimer		<ul style="list-style-type: none"> <li>• Primary and tertiary amines at respective chain ends and branch points.</li> <li>• Regularly ordered highly branched repeating units around a central core.</li> <li>• Size, chemical functionality, and molecular weight can be tuned on demand.</li> <li>• High amine or nitrogen density.</li> </ul>
2.	Polypropylenimine (or polyazetidine)		<ul style="list-style-type: none"> <li>• Better oxidation stability than that of polyethylenimine.</li> <li>• Challenges associated to monomer synthesis and polymerization time.</li> </ul>
2.a.	Linear polypropylenimine		Secondary amines in the back bone.
2.b.	Branched polypropylenimine		Primary, secondary, and tertiary amines at respective chain ends, back bone, and branch points.
2.c.	Polypropylenimine dendrimer		<ul style="list-style-type: none"> <li>• Primary and tertiary amines at respective chain ends and branch points.</li> <li>• Regularly ordered highly branched repeating units around a central core.</li> <li>• Size, chemical functionality, and molecular weight can be tuned on demand.</li> <li>• High amine or nitrogen density.</li> </ul>
2.d.	Hyperbranched polypropylenimine		<ul style="list-style-type: none"> <li>• Primary, secondary, and tertiary amines at respective chain ends, back bone, and branch points.</li> <li>• Irregularly ordered, highly branched macromolecular structure.</li> <li>• High amine or nitrogen density.</li> </ul>

(continued on next page)



Table 1 (continued)

S.No.	Polymeric amine	Chemical structure	Remarks
3.	Polyallylamine		<ul style="list-style-type: none"> <li>• Primary amine at the side chain.</li> <li>• Better thermal and oxidation stabilities.</li> <li>• Capable to bind strongly with other material surfaces.</li> </ul>
4.	Polyaniline		<ul style="list-style-type: none"> <li>• Secondary amines in the backbone.</li> <li>• Superior thermal stability.</li> </ul>

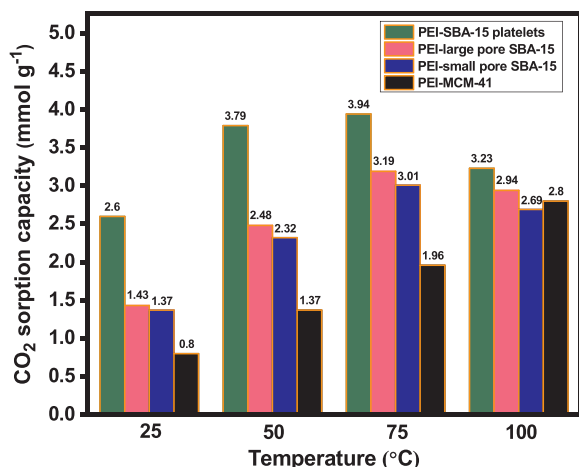


Fig. 2. CO<sub>2</sub> adsorption capacity at 1 bar for PEI - impregnated SBA-15 platelets in comparison to SBA-15 possessing large as well as small pores, and MCM-41.

which was almost analogous to that of neat mesoporous silica at the same conditions. The capacity increased with increase in temperature and a maximal value of ca. 1.55 mmol g<sup>-1</sup> was observed at 75 °C. Yan et al. (Yan et al., 2013) made use of PEI with  $M_n$  of 600 for the modification of SBA-15. At 273 K and 800 mmHg, an adsorption capacity of more than 1.8 mmol g<sup>-1</sup> was realized for 20 wt% PEI - modified SBA-15. Heydari-Gorji et al. (Heydari-Gorji et al., 2011b) reported higher adsorption capacities of ca. 2.60 and 3.94 mmol g<sup>-1</sup> at 25 and 75 °C, respectively and 1 atm, for 55 wt% PEI - impregnated in SBA-15 platelets in comparison to SBA-15 possessing small and large pores and MCM-41 (Fig. 2). Holewinski et al. (Holewinski et al., 2015) studied PEI dispersion on the SBA-15 pore walls paying attention to coating formation at initial composition and then deposition upon increase in PEI amount. Wang et al. (Wang et al., 2009) emphasized that effective anchoring of PEI into mesoporous SBA-15 was possible by means of amine-silanol interactions.

Sanz-Perez et al. (Sanz-Pérez et al., 2013) evaluated the CO<sub>2</sub> adsorption performance of PEI - modified SBA-15 in simulated post-combustion ambiances. The adsorption capacity of 50 wt% PEI - modified SBA-15 remained almost unaffected for up to 10 adsorption/desorption cycles in diluted CO<sub>2</sub> gas mixtures, whereas some reduction was noticed for tetraethylenepentamine - modified SBA-15. Under the presence of 1000 ppm SO<sub>2</sub>, the adsorption capacity of the aforementioned adsorbents was considerably decreased. Additionally, owing to the substantial amount of nitrogen occupancy, PEI - modified SBA-15 displayed an increase by ca. 60 % in adsorption capacity under moisture influence (5 %). In another work, Sanz-Perez et al. (Sanz-Pérez et al., 2017) investigated the reusability of PEI - impregnated SBA-15 based CO<sub>2</sub> adsorbents. For this, the authors followed repeated calcination/re-functionalization cycles. After 7 such cycles, PEI - impregnated SBA-15 was found to maintain to a good extent its initially obtained adsorption capacity (1.72 mmol g<sup>-1</sup> under 1 bar and 45 °C). This observation was related to the amine efficiency, typically defined as the moles of CO<sub>2</sub> adsorbed normalized by the moles of amine present in the material, after each PEI loading cycle. Yan et al. (Yan et al., 2011b) also

underlined the capability of SBA-15 supported PEI based solid CO<sub>2</sub> adsorbents to maintain their adsorption capacity upon cyclic adsorption-desorption operation.

With an objective to further enhance CO<sub>2</sub> uptake, Sanz et al. (Sanz et al., 2013) reported the dual amine modification of pore-expanded SBA-15. To achieve this, the researchers carried out an initial (3-aminopropyl)triethoxysilane (APTES) grafting followed by PEI impregnation. The application of dual modification was found to be advantageous for CO<sub>2</sub> capture due to the increase in amine content and efficiency. Specifically, an enhanced CO<sub>2</sub> uptake of ca. 2.80 mmol g<sup>-1</sup> was observed at 1 bar and 45 °C for pore-expanded SBA-15 modified with 6.87 mmol APTES and 50 wt% PEI, though, the adsorption kinetics of such solid sorbent displayed a reduction trend. Similarly, Sakwa-Novak et al. (Sakwa-Novak et al., 2015b) studied the effect of poly (ethylene glycol) (PEG) addition on the performance of PEI - impregnated SBA-15 adsorbent. The infusion of PEG with an average molecular weight of 200 resulted in ca. 60 % performance enhancement.

Cheng et al. (Cheng et al., 2015) observed that the introduction of phosphate ester surfactants such as bis(2-ethylhexyl)phosphate and tri (2-ethylhexyl)phosphate (TEHP) was beneficial to enhance the CO<sub>2</sub> adsorption of SBA-15 supported PEI. Indeed, the CO<sub>2</sub> capture capacity for SBA-15 with 45 % PEI and 5 % TEHP at 75 °C and 1 atm was 1.89 mmol g<sup>-1</sup>, which was ca. 19 % higher compared to the same adsorbent without the added surfactant. Liu et al. (Liu et al., 2013a) reported that propanesulfonic acid surface treatment enhanced the performance of SBA-15 after PEI - loading by improving dispersion and increasing CO<sub>2</sub> diffusion. Adsorption studies in a gravimetric analyzer revealed an optimal capacity of ca. 2.30 mmol g<sup>-1</sup> at 75 °C and 1 atm, for SBA-15/PEI composite sorbent treated with 5 % propanesulfonic acid. The increased acidity of the support surface and stronger interaction with the amines, resulted in enhanced flexibility in adsorbent regenerability compared to the unmodified material.

Kuwahara et al. (Kuwahara et al., 2012b) investigated the influence of various heteroatoms such as Al, Ti, Zr, and Ce on the CO<sub>2</sub> adsorption of SBA-15 supported BPEI ( $M_w$  = 800). The maximal CO<sub>2</sub> adsorption capacities of ca. 1.56 and 1.68 mmol g<sup>-1</sup> was observed for the Zr containing sorbent in dry and humid conditions, respectively, for 10 % CO<sub>2</sub> at 25 °C. Investigating the effect of Zr loading, 7 mol% Zr showed an optimal performance in terms of adsorption capacity and amine efficiency (Kuwahara et al., 2012a). Sakwa-Novak et al. (Sakwa-Novak et al., 2015a) also reported the advantage of Zr infusion in enhancing the CO<sub>2</sub> performance of PEI - impregnated SBA-15. Indeed, an increase of ca. 60 % in adsorption capacity was obtained by Zr doping of SBA-15, though, Zr doping had no significant influence on the adsorption performance of SBA-15 with large pores.

According to above results, a capture capacity of SBA-15 platelets - supported PEI sorbent is highlighted, i.e. 3.94 mmol g<sup>-1</sup> (Heydari-Gorji et al., 2011b), as well as of conventional SBA-15 - supported LPEI of 3.51 mmol g<sup>-1</sup> (Wang et al., 2013c) together with good conservation of mesoporosity. Moreover, propanesulfonic acid - treated SBA-15 - supported PEI sorbent presents improved regenerability and capacity maintenance (2.3 mmol g<sup>-1</sup>) (Liu et al., 2013a) on account of increased surface interaction with the amines. It has also been observed that dual amine modification of pore-expanded SBA-15 by APTES and BPEI is

beneficial to enhance amine efficiency and, as a result, an improved capacity was reported (e.g.  $2.8 \text{ mmol g}^{-1}$ ) accompanied with a reduction of sorption kinetics (Sanz et al., 2013). It is evident from these observations that more attempts are needed to precisely optimize the performance of SBA-15 supported PEI  $\text{CO}_2$  capture sorbents by studying different systems based on SBA-15 with varying morphological and surface features, PEI with varying concentration, molecular weight and structural features, combination or blending with other amines, and doping or incorporation of other additives. Moreover, the effect of *in situ* PEI functionalization on the performance of SBA-15 could be explored as well.

### 2.1.2. MCM-41 – supported PEI

Since its development in 1992 by Beck et al. (Beck et al., 1992) in Mobile Research and Development Corporation, MCM-41 (Mobil Composition of Matter No. 41, also known as Mobil Crystalline Material No. 41) has received considerable attention in various applications with main focus on catalysis (Diaz and Balkus, 1996; Trewyn et al., 2007; Vallet-Regi et al., 2001), as it constitutes a structure of the class of ordered mesoporous silica materials with uniformly ordered honeycomb like pores with diameter in the range of 2–6.5 nm. Interestingly, the size and distribution of the mesopores can be tailored by demand (Beck et al., 1992; Chen et al., 1993a, b; Kresge et al., 1992; Schmidt et al., 1995). Due to these features, MCM-41 is extensively being investigated for  $\text{CO}_2$  capture applications as well.

Ahmed et al. (Ahmed et al., 2017) reported the preparation of  $\text{CO}_2$  adsorbent by means of effective BPEI loading into mesoporous MCM-41. Of the various compositions studied, 50 wt% BPEI loading demonstrated the maximum adsorption capacity of ca.  $2.26 \text{ mmol g}^{-1}$  at 1 bar and  $100^\circ\text{C}$ . The authors also studied the effect of increase in pressure until 20 bar, and found an increased capacity of ca.  $3.55 \text{ mmol g}^{-1}$ , as portrayed in Fig. 3. High  $\text{CO}_2/\text{N}_2$  and  $\text{CO}_2/\text{H}_2$  selectivities were also reported for this adsorbent. A reduction in adsorption capacity after 3 and 6 cycles by ca. 9.29 and 21.68 %, respectively, was also observed.

Le et al. (Le et al., 2014) carried out PEI impregnation of MCM-41 mesoporous silica using different PEI amounts in the range of 10–60 wt%. An optimal  $\text{CO}_2$  adsorption capacity of ca.  $0.57 \text{ mmol g}^{-1}$  was discerned for 50 wt% PEI ( $M_w = 25,000$ ), as revealed by gravimetric adsorption studies at  $40^\circ\text{C}$ . The aforesaid result was related to the influence of higher N content by ca. 17 %, which offered improved acid-base reaction with  $\text{CO}_2$ . In addition, X-ray diffraction (XRD) underlined the PEI dispersion in the MCM-41 framework by displaying a down-shifting of the characteristic diffraction peak corresponding to (110) plane. Concerning the pore volume and surface area of MCM-41, a

decreasing trend was observed with increase in PEI loading.

Boonpoke et al. (Boonpoke et al., 2016) carried out PEI functionalization on rice husk sourced MCM-41 and compared its performance with aniline- and monoethanolamine - modified systems. Of the studied adsorbents, PEI - functionalized MCM-41 showed better  $\text{CO}_2$  capture performance, namely, a capture capacity of ca.  $1.70 \text{ mmol g}^{-1}$  was obtained for 50 wt% PEI loading at  $75^\circ\text{C}$ . Liu et al. (LIU et al., 2013b) compared two different PEI molecular weights i.e., 600 and 1800, on the modification of MCM-41. In this study, the modified material with lower molecular weight PEI displayed superior adsorption capacity in comparison to one with higher molecular weight. Specifically, adsorption capacities of ca. 1.6 and  $1.3 \text{ mmol g}^{-1}$  were obtained at  $35^\circ\text{C}$  and 10 %  $\text{CO}_2$  for low and high molecular weight PEI - impregnated systems, respectively, with a loading amount of 40 wt%. Furthermore, the cyclic and thermal stabilities were higher for PEI - modified systems regardless of their molecular weight when compared to tetraethylenepentamine - modified one.

In order to ensure effective post-combustion  $\text{CO}_2$  capture, research performed by Sanz et al. (Sanz et al., 2015) accounted the dual amine modification of pore-expanded MCM-41. Dual amine modification was found to exhibit enhanced amine efficiency and adsorption capacity. Indeed, adsorption studies performed at  $45^\circ\text{C}$  and 1 bar revealed adsorption capacities of 1.39 and  $1.80 \text{ mmol g}^{-1}$  and amine efficiencies of 0.35 and 0.30 mol  $\text{CO}_2/\text{mol N}$  for aminopropyl/PEI- and diethylenetriamine/PEI - modified MCM-41, respectively. Heydari-Gorji et al. (Heydari-Gorji and Sayari, 2011) reported the preparation of  $\text{CO}_2$  adsorbent through impregnation of PEI into mesoporous silica MCM-41 with cetyltrimethylammonium modification. The modified adsorbent comprising 55 wt% of PEI ( $M_n = 423$ ) showed a  $\text{CO}_2$  adsorption capacity as high as  $4.69 \text{ mmol g}^{-1}$  at  $75^\circ\text{C}$  and 1 atm. In an analogous study, Sayari et al. (Sayari et al., 2016) reported a higher  $\text{CO}_2$  adsorption capacity for cetyltrimethylammonium - treated pore-expanded MCM-41 after PEI impregnation by virtue of increased amine efficiency. Specifically, adsorption capacities of ca. 2.2 and  $2.9 \text{ mmol g}^{-1}$  were observed at  $25^\circ\text{C}$  and ambient pressure for 40 wt% PEI - loaded support after cetyltrimethylammonium treatment in dry and humid conditions, respectively. Furthermore, the adsorption capacity was found to decrease by 4.6 % after 20 adsorption-desorption cycles under dry conditions, whereas a 2 % decrease was noted under humid environment.

It is worth noting that cetyltrimethylammonium modification of conventional as well as pore-expanded MCM-41 is beneficial to enhance the performance of MCM-41 supported PEI  $\text{CO}_2$  sorbents, and indicatively a capacity of  $4.69 \text{ mmol g}^{-1}$  was achieved (Heydari-Gorji and Sayari, 2011). It is evident that more surface modifications of MCM-41 need to be realized as to optimize performance, while the practicability of *in situ* synthesis of PEI over MCM-41 support can be considered in future activities.

### 2.1.3. Fumed silica – supported PEI

Fumed silica ( $\text{SiO}_2$ , also named as pyrogenic silica) is a class of nonporous pure silica possessing large surface area of ca.  $600 \text{ m}^2 \text{ g}^{-1}$  and particle size range of 5–50 nm. For  $\text{CO}_2$  capture, fumed silica based supported adsorbents have displayed promising performance as a result of the relatively large surface area in combination with good adsorption capacity and selectivity, but also with superior mechanical performance (Florke et al., 2008; Pevida et al., 2008a; King and Ho, 2011).

Zhang et al. (Zhang et al., 2015) reported the generation of LPEI - coated fumed silica based  $\text{CO}_2$  adsorbents using the wet impregnation approach. The resulting adsorbent displayed high selectivity even in dry air condition. An optimal  $\text{CO}_2$  adsorption capacity of ca.  $3.53 \text{ mmol g}^{-1}$  was reported for this system at  $25^\circ\text{C}$ . In addition, LPEI - coated fumed silica offered benefits in terms of faster desorption potential in the temperature range of 50– $100^\circ\text{C}$ . Interestingly, the adsorption capacity of this adsorbent remained stable even after > 100 adsorption-desorption cycles. As compared to BPEI - coated system, LPEI - coated fumed

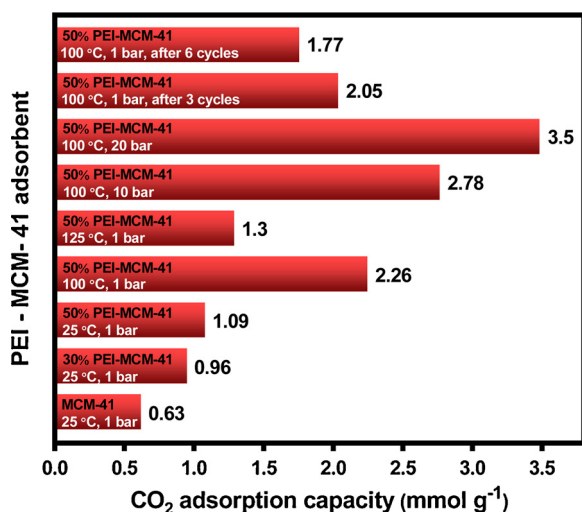


Fig. 3.  $\text{CO}_2$  adsorption capacity for PEI - impregnated MCM-41 in varying conditions.

silica displayed substantially lower values of heat of adsorption.

Geoppert et al. (Goepfert et al., 2011) studied the CO<sub>2</sub> adsorption behavior of BPEI - functionalized fumed silica. An adsorption capacity of 1.74 mmol g<sup>-1</sup> at 25 °C and 1 atm, was observed in humid conditions after impregnation using 33 wt% BPEI. This material also offered reasonable regenerability over repeated adsorption-desorption cycles. Yoosuk et al. (Yoosuk et al., 2016) reported a capture capacity of 2.57 mmol g<sup>-1</sup> at 80 °C, for 10 % CO<sub>2</sub>/N<sub>2</sub> mixture by using fumed silica supported PEI ( $M_w$  = 800) with 40 wt% of PEI loading.

Zhang et al. (Zhang et al., 2017a) studied the effect of moisture on the adsorption performance of PEI - loaded fumed silica. From the experimental data, it was clear that the influence of up to 11.5 mg H<sub>2</sub>O g<sup>-1</sup> specific humidity had a positive effect on the adsorption capacity for both BPEI- and LPEI - loaded systems at a temperature of 25 °C. Further increase of specific humidity had no significant effect on the adsorption capacity of LPEI based systems, whereas a reversing effect was observed in the case of BPEI. An optimal adsorption capacity of ca. 4.1 mmol g<sup>-1</sup> was reported for 44.5 wt% LPEI - loaded fumed silica under the influence of 15.3 mg H<sub>2</sub>O g<sup>-1</sup>, as compared to ca. 1.4 mmol g<sup>-1</sup> in dry CO<sub>2</sub>.

Zhang et al. (Zhang et al., 2017b) compared the CO<sub>2</sub> adsorption capacity of PEI - loaded fumed silica with that of PEI - loaded 3D TUD-1 and 2D SBA-15. Gravimetric adsorption at 95 °C and atmospheric pressure revealed that the maximum value of adsorption capacity of ca. 3.07 mmol g<sup>-1</sup> was recorded for 40 wt% PEI - loaded fumed silica. Interestingly, the addition of PEG into the aforesaid molecular basket CO<sub>2</sub> sorbent further strengthened its capacity through the increase of amine efficiency by causing stronger inter-molecular affinity with bulk PEI. As a result, PEI layer separation was increased thus facilitating diffusion, as depicted schematically in Fig. 4.

Wang et al. (Wang and Song, 2014) followed a modified approach to enhance the performance of molecular basket CO<sub>2</sub> sorbent based on PEI - modified fumed silica by changing the reaction chemistry upon adsorption. For this purpose, the researchers enabled infusion of potassium carbonate in order to increase amine efficiency and adsorption capacity by shifting the corresponding chemisorption stoichiometric value from 2 to 1. Thus, an increased capacity of ca. 2.73 mmol g<sup>-1</sup> was yielded at atmospheric pressure and 75 °C, along with enhanced

regenerability.

In an interesting study, Du et al. (Du et al., 2013) carried out PEI functionalization of poly(acrylic acid) (PAAcid) - modified fumed silica. In this system, PAAcid functioned as multifaceted bridge where the attached carboxylic acid groups were effectively reacted with amine groups from PEI. The effect of molecular weights of PEI and PAAcid on the CO<sub>2</sub> uptake of the resultant sorbent system was evaluated, and the results indicated superior performance for fumed silica - modified with higher molecular weight PEI and PAAcid. A CO<sub>2</sub> capacity of 3.8 mmol g<sup>-1</sup> at 40 °C and 1 atm, was realized for the adsorbent containing PAAcid and PEI with molecular weights of 3000 and 10,000, respectively. Zhu et al. (Zhu and Baker, 2014) studied the influence of three different modifiers based on Lewis-base polymers on the adsorption behavior of BPEI ( $M_w$  = 25,000) - functionalized fumed silica. Gravimetric adsorption studies at 45 °C and 1 bar revealed that PEG had a positive effect on the adsorption capacity in comparison to other modifiers such as poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAC), while PMMA and PVAC modifiers offered advantages in terms of desorption kinetics and regenerability.

The above studies pointed out that PAAcid modification of fumed silica is a promising approach to enhance the performance of fumed silica supported PEI CO<sub>2</sub> sorbent and indicatively an capacity of 3.8 mmol g<sup>-1</sup> (Du et al., 2013) was observed, whereas the highest capacity for conventional fumed silica supported PEI was 3.53 mmol g<sup>-1</sup> (Zhang et al., 2015) among the various studies. Available reports show that more attempts have to be generated to precisely study adsorption properties other than capacity, as well as effectiveness of *in situ* synthesis of PEI over fumed silica support.

#### 2.1.4. Precipitated silica – supported PEI

Precipitated or amorphous silica is an interesting class of mesoporous silica having particle sizes in the range of 5–100 nm and specific surface area in the order of 100 m<sup>2</sup> g<sup>-1</sup>. Its large pores with > 30 nm pore diameter, increased surface area, and comparatively low cost make it suitable for large scale applications related to CO<sub>2</sub> capture (Ichikawa et al., 2010; Quang et al., 2013, 2015).

Li et al. (Li et al., 2014) made comparisons between LPEI- and BPEI - modified precipitated silica for CO<sub>2</sub> adsorption. The BPEI - modified

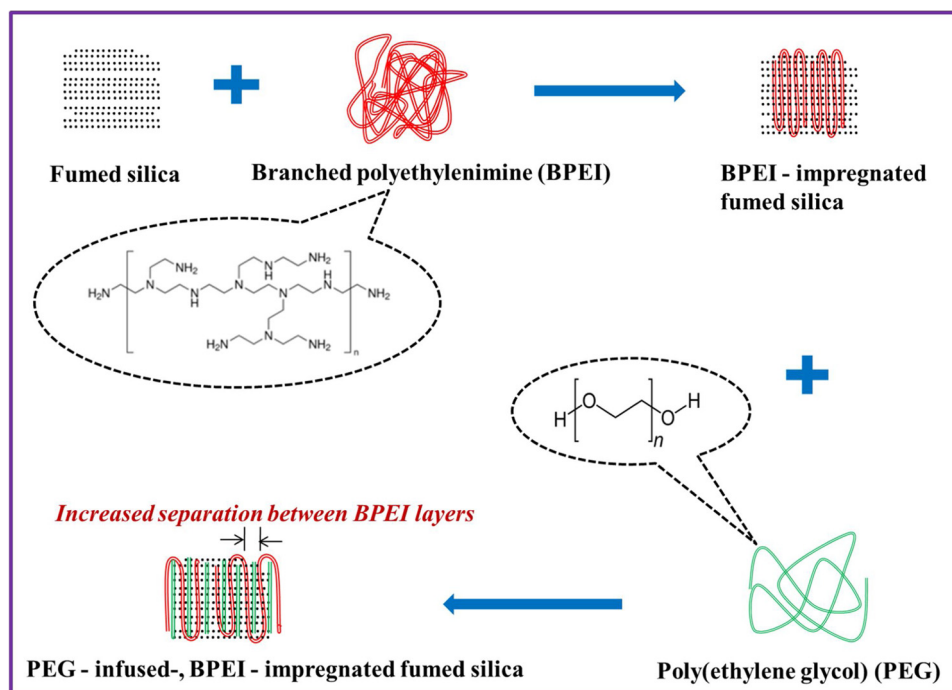


Fig. 4. Schematic representation of the role of PEG addition on the structure of PEI - impregnated fumed silica.



material exhibited a higher CO<sub>2</sub> capacity than that of the LPEI - modified one. A capacity of ca. 4.60 mmol g<sup>-1</sup> was realized for precipitated silica functionalized using BPEI with a molecular weight of 800 at 105 °C, though, LPEI - modified precipitated silica displayed a superior adsorption-desorption cycling stability. Additionally, with increase in PEI molecular weight, the adsorption capacity was decreased. In another work, the same team also studied the impact of differing adsorption conditions and BPEI amounts on the CO<sub>2</sub> capacity. Specifically, observed CO<sub>2</sub> capacities included ca. 3.05 mmol g<sup>-1</sup> at 0.15 bar and 75 °C and 3.64 mmol g<sup>-1</sup> at 1 atm and 90 °C for 50 wt% BPEI, and 3.01 mmol g<sup>-1</sup> at 0.15 bar and 75 °C and 4.24 mmol g<sup>-1</sup> at 1 atm and 105 °C for 60 wt% BPEI (Li et al., 2015). Quang et al. (Quang et al., 2013) reported a reduced regeneration energy for precipitated silica-supported BPEI ( $M_w = 1300$ ). For such sorbent with 50 wt% BPEI, a reduction of ca. 46.7 % was accomplished as compared to a 30 % methanolamine aqueous solution.

As compared to silica materials that were discussed in the previous sections, precipitated silica supported PEI CO<sub>2</sub> sorbent showed enhanced performance in its conventional form, with indicatively a capture capacity of 4.60 mmol g<sup>-1</sup> (Li et al., 2014). The limited reports on precipitated silica supported PEI sorbents directs for more detailed investigations by exploring various key parameters such as support material pre-modification approaches, incorporation of different modifiers and dopants, *in situ* generation of PEI, effect of various PEI materials and concentrations.

### 2.1.5. Mesoporous siliceous foam – supported PEI

For CO<sub>2</sub> capture applications, mesoporous siliceous foam can be considered as one of the strong candidates from the family of porous siliceous materials. Mesoporous siliceous foam is a hierarchical interconnected cellular nanostructured version of silica with pore diameters in at least 2–3 different scales in the range of 0.2–50 nm. In addition to this, the presence of large surface area, and tailorable pore and window dimensions by varying the synthesis approach, make such material suitable as support for effective CO<sub>2</sub> capture (Jeon et al., 2015; Lukens et al., 2001; Sen et al., 2005).

Research conducted by Subagyono et al. (Subagyono et al., 2011) revealed the potential of BPEI - impregnated mesocellular siliceous foam possessing highly ordered mesoporosity and substantial surface area for CO<sub>2</sub> adsorption applications at higher temperatures. For a 70 wt% BPEI - impregnated system, the observed adsorption capacity values were ca. 3.44 mmol g<sup>-1</sup> at 105 °C and 3.03 mmol g<sup>-1</sup> at 115 °C in a gas mixture of 50 % CO<sub>2</sub>-Ar. The observed values were higher compared to a system based on same amount of BPEI - impregnated in SBA-15. Moreover, with increase in temperature, the adsorption-desorption kinetics improved, whereas the capacity was decreased. In another work, Zhao et al. (Zhao et al., 2012a) compared the effect of PEI impregnation on the CO<sub>2</sub> adsorption capacity of mesoporous siliceous foam. The porosity of the siliceous foam was observed to be within the range of 1.12–1.64 cm<sup>3</sup> g<sup>-1</sup> after impregnation of PEI. A maximum adsorption capacity of ca. 4.11 mmol g<sup>-1</sup> was acquired at 75 °C after impregnation of 50 wt% of BPEI with  $M_w$  of 600 in comparison to BPEI and LPEI with  $M_w$  of 25,000.

Zhang et al. (Zhang et al., 2014a) also reported the generation of CO<sub>2</sub> adsorbents based on mesoporous siliceous foam with PEI impregnation using different molecular weights and amounts. According to the obtained results, the designed adsorbents corresponding to 50 % BPEI loading and  $M_w$  of 800 exhibited large pore volume (ca. 4.17 cm<sup>3</sup> g<sup>-1</sup>) and an optimal value of CO<sub>2</sub> uptake of ca. 6 mmol g<sup>-1</sup> at 85 °C. Interestingly, the adsorption kinetics was high for the adsorbent comprised of PEI with  $M_w$  of 25,000 compared to PEI with  $M_w$  of 800. Considering regenerability, the resulting adsorbents possessed superior stability independently of PEI molecular weight for more than 100 consecutive adsorption/desorption cycles at 75 °C.

Liu et al. (Liu et al., 2015b) further reported on the suitability of PEI - impregnated mesoporous silica foam for effective capture of CO<sub>2</sub> from

flue gas. Therein, gravimetric adsorption studies at 75 °C and 1 atm, revealed a superior performance for the adsorbent corresponding to 70 wt% PEI, with capacities of ca. 5 and 4 mmol g<sup>-1</sup> for 10 % and 95 % CO<sub>2</sub>/N<sub>2</sub> mixtures, respectively. Notably, the adsorption capacity of this system was observed to significantly increase under the influence of humidity. Additionally, after 50 successive adsorption-desorption cycles, this system demonstrated appreciable regenerability. In another work, Knowles et al. (Knowles et al., 2017) introduced composite pellets of PEI - loaded mesoporous siliceous foam as CO<sub>2</sub> adsorbents. The optimal PEI loading was found to be 71.2 wt% with an adsorption capacity of 0.9 mmol g<sup>-1</sup> at 105 °C, which was found to be maintained upon regeneration. To enhance uptake, the positive effect of sonication upon synthesis of BPEI ( $M_w = 1200$ ) - impregnated mesocellular silica foam was highlighted by Wijesiri et al. (Wijesiri et al., 2019) by means of improvement in PEI dispersion and infiltration. A CO<sub>2</sub> capacity of 1.94 mmol g<sup>-1</sup> was recorded at 46 °C and atmospheric pressure, whereas the respective value without sonication was 1.29 mmol g<sup>-1</sup>. Al-Marri et al. (Al-Marri et al., 2015) revealed the existence of a higher CO<sub>2</sub> uptake capacity for mesocellular siliceous foam functionalized using LPEI ( $M_n = 423$ ) in comparison to BPEI ( $M_n = 10,000$ ), though, the observed thermal stability was superior for the BPEI - based system.

Qi et al. (Qi et al., 2012) reported on the effectiveness of PEI filling of very large mesopores (> 40 nm) of structured silica foam. In this study, low molecular weight PEI ( $M_w = 423$ ) was more efficient in terms of adsorption capacity, whereas high molecular weight PEI ( $M_w = 10,000$ ) displayed more regeneration stability upon repeated adsorption/desorption cycles. Specifically, a high adsorption capacity of ca. 5.8 mmol g<sup>-1</sup> was achieved at 1 atm and 75 °C for 80 wt% low molecular weight PEI in dry CO<sub>2</sub> environment, with the adsorbents exhibiting also fast adsorption/desorption kinetics. Another research reported by Yan et al. (Yan et al., 2011a) demonstrated a trend of increase in adsorption capacity with increase in pore size for LPEI - modified silica mesoporous foam. Therein, an adsorption capacity of ca. 3.46 mmol g<sup>-1</sup> was observed at atmospheric pressure and 75 °C for a 15.1 % CO<sub>2</sub>/N<sub>2</sub> mixture after impregnation with 50 wt% LPEI of  $M_w$  of 423 into mesoporous silica foam. Good regenerability was also observed for this adsorbent after repeated cycles of adsorption and desorption.

Wang et al. (Wang et al., 2014a) compared the CO<sub>2</sub> adsorption behavior of PEI - modified 3-dimensional siliceous mesoporous foam with that of 2- and 1-dimensional materials, and they showed superior performance in terms of capacity and kinetics for the former system. An adsorption capacity of ca. 4.58 mmol g<sup>-1</sup> was reported as the maximum value after the infusion of 65 wt% PEI ( $M_n = 423$ ) into 3-dimensional siliceous mesoporous foam at 75 °C and atmospheric pressure. In another work, Vilarrasa-Garcia et al. (Vilarrasa-Garcia et al., 2015) reported an uptake of ca. 2.3 mmol g<sup>-1</sup> at 25 °C and 1 bar for 50 wt% PEI - impregnated in highly disordered siliceous mesocellular foams, which was higher than other siliceous mesoporous materials.

Yan et al. (Yan et al., 2012) reported the design of an effective CO<sub>2</sub> adsorbent through the PEI introduction into poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) triblock copolymer (Pluronic P123) - attached mesocellular silica foam possessing not only high adsorption capacity but also enhanced thermal stability. Gravimetric adsorption studies at 70 °C revealed an adsorption capacity of 4.45 mmol g<sup>-1</sup> for the adsorbent corresponding to 60 % of PEI. Concerning stability, the system exhibited almost constant adsorption capacity after 10 consecutive cycles of adsorption/desorption, also exhibiting high CO<sub>2</sub>/N<sub>2</sub> selectivity. In addition, through the Langmuir isotherms, an adsorption enthalpy of  $-85 \text{ kJ mol}^{-1}$  was resulted, which supports a chemical - based adsorption mechanism through the interaction of amines with Pluronic P123 micelles.

The modification of mesoporous silica foam through infusion of PEI and PEI blends with other amines like diethylenetriamine and 3-aminopropyltrimethoxysilane (APTMS) was reported by Ma et al. (Ma et al., 2014). The existence of the Pluronic P123 template in the silica



foam had an enhancing effect on the CO<sub>2</sub> capture. As a result, a CO<sub>2</sub> uptake of ca. 3.24 mmol g<sup>-1</sup> was yielded at 85 °C and 1 atm, for a PEI loading of 70 %. The adsorbents based on blends, owing to the increased dispersion of PEI, demonstrated higher capacity values than that of PEI alone at the same conditions. PEI/APTMS was more effective to exhibiting an adsorption capacity of ca. 2.67 mmol g<sup>-1</sup> at 50 °C and 1 atm.

In order to improve cyclic as well as thermal stability on CO<sub>2</sub> adsorption applications, Jung et al. (Jung et al., 2017) studied the effectiveness of crosslinked PEI. Therein, the authors reported the modification of mesocellular silica foam through the use of 1,3-butadiene diepoxide crosslinked 50 wt% PEI. PEI crosslinking was found to reduce the tendency of urea evolution due to formation of secondary amines than primary ones as well as hydroxyl group formation. In another work, Jeon et al. (Jeon et al., 2017) also found out a similar kind of suppression of urea evolution trend for adsorbents based on crosslinked PEI - impregnated mesoporous silica foam. The authors used glyoxal solution and oxalic acid as crosslinking agents. Though, the observed CO<sub>2</sub> adsorption capacity of crosslinked PEI - modified system was lower than that of PEI - modified system.

The increased number of research activities on silica foam supported PEI CO<sub>2</sub> sorbents indicates the superior properties of this material leading to high capacity values (6 mmol g<sup>-1</sup> indicatively (Zhang et al., 2014a)). Effective tuning of textural features of a silica foam support may lead to further optimization. Furthermore, precise investigation on surface pre-modification of silica foam is needed, whereas only few studies reported the role of pluronic P123 involvement. The role of different modifiers and dopants as well as addition of other amines on the final performance needs to be studied in detail. Also, it would be appreciable to compare the performance of silica foam supported PEI sorbent with that of an analogous adsorbent synthesized and functionalized *in situ*.

#### 2.1.6. Silica gel – supported PEI

Silica gel is an amorphous form of silica with irregular pattern of nanopores in the range of 2.4–7 nm. Due to its pore structure along with relatively large surface area of ca. 800 m<sup>2</sup> g<sup>-1</sup> and low cost, silica gel has been investigated as support for CO<sub>2</sub> sorption applications (Anderson and Parks, 1968; Sharp, 1994; Wurzbacher et al., 2011).

Cost effective adsorbent composed of PEI - impregnated silica gel was prepared by Zhang et al. (Zhang et al., 2012), who observed higher CO<sub>2</sub> uptake when compared to SBA-15 supported PEI. Accordingly, a mass-based uptake of 3.14 mmol/g and a volume-based uptake of 83 mg/cm<sup>3</sup> were obtained at 75 °C for silica gel - loaded by 50 wt% of PEI. In another study, Wang et al. (Wang et al., 2012a) also reported the preparation of silica gel/PEI adsorbent and achieved a CO<sub>2</sub> uptake of ca. 2.13 mmol g<sup>-1</sup> at atmospheric pressure and 70 °C, for 30 wt% LPEI ( $M_w = 423$ ) using a 15.1 % CO<sub>2</sub>/N<sub>2</sub> mixture. The capacity remained almost unchanged for > 5 cycles of operation. For 20 wt% PEI - impregnated silica gel, Sakpal et al. (Sakpal et al., 2012) observed an uptake of 4.69 mmol g<sup>-1</sup> in 99.99 % CO<sub>2</sub> at 275 K and 3.5 MPa. The authors also made a comparison with the APTES - modified system and found a higher performance for the PEI based system due to the higher amine density.

Quang et al. (Quang et al., 2016) also carried out PEI functionalization of silica gel for CO<sub>2</sub> capture. Among the modified systems obtained using differing amounts of BPEI ( $M_w = 600$ ), the one with 40 wt % polymer demonstrated optimal performance in terms of adsorption capacity, i.e. ca. 2.44 mmol g<sup>-1</sup> at 65 °C in simulated flue gas passing through a packed bed reactor. In addition, high stability was observed over repeated adsorption-desorption cycles for this adsorbent in a fluidized bed reactor. Zhang et al. (Zhang et al., 2014c) reported the use of PEI - modified fly ash sourced silica gel. At a pressure of 0.5 bar, the resultant PEI - modified silica gel displayed good adsorption capacities of ca. 3.18 and 3.30 mmol g<sup>-1</sup> at 75 and 90 °C, respectively. This system exhibits good potential in terms of stability, cost effectiveness,

and waste management.

Zhao et al. (Zhao et al., 2013) studied the thermal degradation behavior of silica gel - supported PEI CO<sub>2</sub> adsorbents. It was found that the thermal stability of these adsorbents was increased with PEI molecular weight. According to the observations, after 10 cycles of operation at 105 °C, the CO<sub>2</sub> uptake capacity of the studied samples remained almost unaffected. In addition, the observed thermal stability of such CO<sub>2</sub> sorbents was higher in a fluidized bed in comparison to gravimetric mode of operation.

The application of diethanolamine together with PEI into silica gel enhanced CO<sub>2</sub> performance (Fan et al., 2019). Accordingly, a capacity of 2.93 mmol g<sup>-1</sup> along with an amine efficiency of 0.40 mol CO<sub>2</sub>/mol N were reported at 35 °C for 50 wt% PEI ( $M_w = 800$ )/diethanolamine (1:1) - loaded silica gel. In the case of neat PEI-silica gel, the respective values were 1.92 mmol g<sup>-1</sup> and 0.17 mol CO<sub>2</sub>/mol N. The observed performance of the developed adsorbent was maintained to a good extent over two cycles of adsorption/desorption.

It has been recognized from above reports that appreciable performance for conventional silica gel - supported PEI CO<sub>2</sub> capture sorbents can be achieved (indicative capacity value of 4.69 mmol g<sup>-1</sup> (Sakpal et al., 2012)) and stability over cyclic operations, in comparison to conventional SBA-15 and MCM-41 based sorbents. The scope of silica gel pre-modification as well as mixed amine infusion on the performance of the sorbents needs to be investigated. Moreover, the subject of *in situ* polymerization of ethylenimine over silica gel support has to be considered.

#### 2.1.7. Other siliceous materials – supported PEI

In this section, we are dealing with studies reported on various PEI - functionalized siliceous CO<sub>2</sub> sorbents that are not discussed in the above categories, namely, KIL-2, KIT-6, other micropores silica grades, macroporous silica, hierarchical bimodal meso-/microporous silica, silica monoliths, silica microspheres, silica hollow microspheres, TUD-1 mesoporous sponge, multilamellar silica vesicles, and silicate magadiite. Summarized CO<sub>2</sub> adsorption properties of various siliceous - based materials are provided in Table 2.

Ojeda et al. (Ojeda et al., 2017) carried out modification of KIL-2 mesoporous silica using PEI with a molecular weight ( $M_w$ ) of 800, and compared its performance with the tetraethylenepentamine - modified system. Results obtained after adsorption studies at 1 bar revealed capacities of ca. 2.19 and 3.60 mmol g<sup>-1</sup> at 25 and 75 °C, respectively, for the PEI - modified KIL-2. Kishor et al. (Kishor and Ghoshal, 2016) used three PEIs which different molecular weight to develop a series of functionalized KIT-6 3-D mesoporous silica adsorbents. The observations showed the potential of the developed materials for CO<sub>2</sub> capture applications requiring superior selectivity and stability. The thermal stability was increased with increase in molecular weight of PEI, while the adsorbent corresponding to PEI with a  $M_w$  of 800 displayed both high selectivity and capacity of ca. 3.00 mmol g<sup>-1</sup> at 1 atm and 105 °C. The capacity of all studied sorbents was increased with temperature, while the adsorbent made using PEI with  $M_w$  of 25,000 displayed better cyclic stability.

Hoffman et al. (Hoffman et al., 2014) evaluated the CO<sub>2</sub> capture capability of silica - supported PEI and reported a capture capacity of ca. 3.5 mmol g<sup>-1</sup> in 10 % CO<sub>2</sub>/He mixture at 60 °C when a 45 wt% of PEI loading was used. Kim et al. (Kim et al., 2019b) developed a PEI (40 wt%) -mesoporous silica composite adsorbent exhibiting a CO<sub>2</sub> removal efficiency of > 80 % and an uptake of > 6 wt% under dynamic conditions at 65 °C and 300 mm H<sub>2</sub>O in a twin bubbling fluidized bed. Fisher et al. (Fisher and Gray, 2015) studied the regenerability of silica - supported PEI employing more than 100 adsorption-desorption cycles, according to which, the system almost maintained its initial CO<sub>2</sub> uptake capacity of ca. 1.75 mmol g<sup>-1</sup> at 50 °C upon the induced cycles. Zhang et al. (Zhang et al., 2016c) reported a heat of regeneration of 2.46 GJ/tCO<sub>2</sub> for mesoporous silica supported PEI CO<sub>2</sub> adsorbents.

A CO<sub>2</sub> adsorbent possessing high SO<sub>2</sub> selectivity was developed by

**Table 2**  
Summarized adsorption properties for CO<sub>2</sub> sorbents based on various siliceous materials - supported polyethylenimine (PEI: polyethylenimine; LPEI: linear polyethylenimine; BPEI: branched polyethylenimine; APTES: (3-aminopropyl)triethoxysilane; APTMS: (3-aminopropyl)trimethoxysilane; GC: gas chromatography; MS: mass spectrometer).

PEI	Support	Adsorption capacity (mmol g <sup>-1</sup> )	Conditions	Method	Remarks	Reference
60 wt% LPEI ( $M_w = 423$ )	SBA-15	3.51	75 °C, 1 atm, 15 % CO <sub>2</sub> /4.5 % O <sub>2</sub> /N <sub>2</sub> mixture	Fixed-bed flow system	Maintained mesoporosity of SBA-15.	(Wang et al., 2013c)
50 wt% PEI ( $M_n = 423$ )	SBA-15	1.52	75 °C, 1 atm, 1 % CO <sub>2</sub> /0.4 % CO/2.6 % Ar/He mixture	Fixed-bed flow system	<ul style="list-style-type: none"> <li>● Selectivity of 14 in CO<sub>2</sub>/CO and 185 in CO<sub>2</sub>/Ar.</li> <li>● Adsorption stability over 20 cycles.</li> </ul>	(Wang et al., 2012b)
42.86 wt% PEI	SBA-15	1.55	75 °C, 1 atm	Micromeritics ASAP 2020 volumetric instrument	Increase in capacity with temperature from 25 to 75 °C.	(Gargiulo et al., 2014)
20 wt% PEI ( $M_n = 600$ )	SBA-15	1.8	-0.15 °C, 1.05 atm	Quantachrome Autosorb-1 equipment	Higher capacity than that of PEI - impregnated MCM-41.	(Yan et al., 2013)
55 wt% PEI ( $M_n = 423$ )	SBA-15 platelets	3.94	75 °C, 1 atm, 99.99 % CO <sub>2</sub>	Gravimetric	Higher capacity than those of PEI - impregnated SBA-15 with small as well as large pores, and MCM-41.	(Heydari-Gorji et al., 2011b)
BPEI ( $M_w = 800$ ) (same loading amount as SBA-15)	SBA-15	1.72	45 °C, 1 bar, 99.99 % CO <sub>2</sub>	Gravimetric	Stability after 7 calcination/re-functionalization cycles.	(Sanz-Pérez et al., 2017)
6.87 mmol APTES + 50 wt% BPEI ( $M_w = 800$ )	Pore-expanded SBA-15	2.80	45 °C, 1 bar, 99.99 % CO <sub>2</sub>	VTI Scientific Instruments	Increase in amine efficiency and nitrogen amount.	(Sanz et al., 2013)
45 % PEI ( $M_w = 600$ ) + 5 % TEHP (tri(2-ethylhexyl) phosphate)	SBA-15	1.89	75 °C, 1 atm, 9.5 % CO <sub>2</sub> /N <sub>2</sub> mixture	HVPA-100 apparatus Quartz fixed-bed reactor	19 % higher capacity compared to surfactant-free adsorbent.	(Cheng et al., 2015)
66.5 wt% PEI	5 % propanesulfonic acid treated SBA-15	2.30	75 °C, 1 atm, 7 % CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	<ul style="list-style-type: none"> <li>● Increase in interaction between SBA-15 and PEI through increase in surface acidity.</li> <li>● Enhanced regenerability.</li> </ul>	(Liu et al., 2013a)
43 wt% BPEI ( $M_w = 800$ ) + Zr	SBA-15	1.56	25 °C, 1 atm, 10 % CO <sub>2</sub> /Ar mixture	Gravimetric	Increase in amine efficiency with Zr addition.	(Kuwahara et al., 2012b)
50 wt% BPEI ( $M_n = 1800$ )	MCM-41	2.26	100 °C, 1 bar, 99.99 % CO <sub>2</sub>	Rubotherm gravimetric-densimetric apparatus	Increase in capacity with pressure up to 20 bar.	(Ahmed et al., 2017)
50 wt% PEI ( $M_w = 25000$ )	MCM-41	0.57	40 °C, 1 atm, 15 % CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	17 at% increase in N content after PEI impregnation.	(Le et al., 2014)
50 wt% PEI ( $M_w = 25000$ )	Rice husk sourced MCM-41	1.70	75 °C, 99.99 % CO <sub>2</sub>	Tubular reactor connected to MS	-	(Boonpake et al., 2016)
40 wt% PEI ( $M_w = 600$ )	MCM-41	1.6	35 °C, 1 atm, 10 % CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	<ul style="list-style-type: none"> <li>● Better cyclic and thermal stability compared to tetraethylenepentamine - modified system.</li> <li>● Capacity of 1.3 mmol g<sup>-1</sup> for 40 wt% PEI (<math>M_w = 1800</math>) - impregnated MCM-14.</li> </ul>	(Liu et al., 2013b)
Aminopropyl/PEI ( $M_w = 800$ )	Pore-expanded MCM-41	1.39	45 °C, 1 bar, 99.99 % CO <sub>2</sub>	VTI Scientific Instruments HVPA-100 equipment	Amine efficiency of 0.35 mol CO <sub>2</sub> /mol N.	(Sanz et al., 2015)
Diethylenetriamine/PEI ( $M_w = 800$ )	Pore-expanded MCM-41	1.80	45 °C, 1 bar, 99.99 % CO <sub>2</sub>	VTI Scientific Instruments HVPA-100 equipment	Amine efficiency of 0.30 mol CO <sub>2</sub> /mol N.	(Sanz et al., 2015)
55 wt% of PEI ( $M_n = 423$ )	Cetyltrimethylammonium modified MCM-41	4.69	75 °C, 1 atm, 99.99 % CO <sub>2</sub>	Gravimetric	Amine efficiency coupled to good adsorption capacity.	(Heydari-Gorji and Sayari, 2011)
40 wt% PEI ( $M_w = 800$ )	Cetyltrimethylammonium covered pore-expanded MCM-41	2.2	25 °C, 1 atm, 400 ppm CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	<ul style="list-style-type: none"> <li>● Higher capacity of 2.9 mmol g<sup>-1</sup> in humid environment.</li> <li>● 4.6 % decrease in capacity after 20 adsorption-desorption cycles under dry condition, whereas only 2 % decrease under humid environment.</li> </ul>	(Sayari et al., 2016)
LPEI ( $M_n = 5000$ )	Fumed silica	3.53	70 °C, 1 atm, 95 % CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	<ul style="list-style-type: none"> <li>● Stability after more than 100 adsorption-desorption cycles.</li> </ul>	(Zhang et al., 2015)

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Table 2 (continued)

PEI	Support	Adsorption capacity (mmol g <sup>-1</sup> )	Conditions	Method	Remarks	Reference
33 wt% BPEI ( $M_w$ = 25000)	Fumed silica	1.74	25 °C, 99.99 % CO <sub>2</sub>	Horiba VIA-510 CO <sub>2</sub> analyzer equipped with infrared detector GC connected single stage fixed-bed flow system	<ul style="list-style-type: none"> <li>Substantially lower values of heat of adsorption and desorption.</li> </ul>	(Goepfert et al., 2011)
40 wt% PEI ( $M_w$ = 800)	Fumed silica	2.57	80 °C, 10 % CO <sub>2</sub> /N <sub>2</sub> mixture		Reasonable regenerability upon repeated adsorption-desorption cycles.	(Yoosuk et al., 2016)
44.5 wt% LPEI ( $M_w$ = 25000)	Fumed silica	1.4	25 °C, 1 atm, 10 % CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	An optimal capacity of 4.1 mmol g <sup>-1</sup> under the influence of 15.3 mg H <sub>2</sub> O g <sup>-1</sup> .	(Zhang et al., 2017a)
40 wt% BPEI ( $M_n$ = 600)	Fumed silica	3.07	95 °C, 1 atm, 99.99 % CO <sub>2</sub>	Gravimetric	<ul style="list-style-type: none"> <li>Better capacity than those of PEI - loaded 3-dimensional TUD-1- and 2-dimensional SBA-15.</li> </ul>	(Zhang et al., 2017b)
PEI ( $M_w$ = 600) + potassium carbonate	Fumed silica	2.73	75 °C, 1 atm, 15 % CO <sub>2</sub> /4.5 % O <sub>2</sub> /N <sub>2</sub> mixture	Fixed-bed flow sorption system	<ul style="list-style-type: none"> <li>Increase in amine efficiency.</li> <li>Shift in chemisorption stoichiometric value to 1 from 2.</li> </ul>	(Wang and Song, 2014)
PEI ( $M_w$ = 10000)	Poly(acrylic acid) ( $M_w$ = 3000) modified fumed silica	3.8	40 °C, 1 atm, 99.99 % CO <sub>2</sub>	Sorption apparatus equipped with online pressure and temperature transducers	<ul style="list-style-type: none"> <li>Enhanced regenerability.</li> <li>Superior performance for sorbent based on PEI and polyacrylic acid with higher molecular weights.</li> </ul>	(Du et al., 2013)
BPEI ( $M_w$ = 25000) + poly(ethylene glycol) ( $M_w$ = 400)	Fumed silica	1.59	45 °C, 1 atm, 99.99 % CO <sub>2</sub>	Gravimetric	<ul style="list-style-type: none"> <li>Better performance than those of other modifiers like poly(methyl methacrylate) and poly(vinyl acetate).</li> </ul>	(Zhu and Baker, 2014)
BPEI ( $M_w$ = 800)	Precipitated silica	4.60	105 °C, 1 atm, 99.99 % CO <sub>2</sub>	Gravimetric	<ul style="list-style-type: none"> <li>Higher capacity and lower cyclic stability than that of LPEI - modified precipitated silica.</li> </ul>	(Li et al., 2014)
60 wt% BPEI ( $M_w$ = 600)	Precipitated silica	4.24	105 °C, 1 atm, 15 % CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	Capacity of 3.01 mmol g <sup>-1</sup> at 0.15 bar and 75 °C.	(Li et al., 2015)
70 wt% BPEI ( $M_n$ = 1200)	Silica foam	3.44	105 °C, 1 atm, 50 % CO <sub>2</sub> /Ar mixture	Gravimetric	<ul style="list-style-type: none"> <li>Better capacity than that of BPEI - impregnated SBA-15.</li> </ul>	(Subagyo et al., 2011)
50 wt% BPEI ( $M_w$ = 600)	Silica foam	4.11	75 °C, 99.8 % CO <sub>2</sub>	Magnetic suspension balance (Rubotherm)	<ul style="list-style-type: none"> <li>Decrease in capacity and increase in adsorption-desorption kinetics with increase in temperature.</li> </ul>	(Zhao et al., 2012a)
75 % BPEI ( $M_w$ = 800)	Silica foam	6	85 °C, 1 atm, 95 % CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	<ul style="list-style-type: none"> <li>Better capacity than that of LPEI with <math>M_w</math> of 25000.</li> <li>Maintained the porosity of silica foam.</li> </ul>	(Zhang et al., 2014a)
70 wt% BPEI ( $M_w$ = 800)	Silica foam	5	75 °C, 1 atm, 10 % CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	<ul style="list-style-type: none"> <li>Slower adsorption kinetics compared to PEI with <math>M_w</math> of 25000.</li> <li>Superior stability over 100 adsorption-desorption cycles regardless of PEI molecular weight.</li> </ul>	(Liu et al., 2015b)
71.2 wt% BPEI ( $M_w$ = 1200)	Silica foam	0.9	105 °C, 15 % CO <sub>2</sub> /Ar mixture	Gravimetric	<ul style="list-style-type: none"> <li>Capacity of 4 mmol g<sup>-1</sup> in 95 % CO<sub>2</sub>/N<sub>2</sub> mixture.</li> <li>Appreciable regenerability over 50 adsorption-desorption cycles.</li> </ul>	(Knowles et al., 2017)
80 wt% PEI ( $M_w$ = 423)	Silica foam with sizeable mesopores (> 40 nm)	5.8	75 °C, 1 atm, 80 % CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	<ul style="list-style-type: none"> <li>Faster adsorption-desorption kinetics.</li> <li>Lower regenerability than that of PEI with <math>M_w</math> of 10000.</li> </ul>	(Qi et al., 2012)
50 wt% LPEI ( $M_w$ = 423)	Silica foam	3.46	75 °C, 1 atm, 15.1 % CO <sub>2</sub> /N <sub>2</sub> mixture	Packed bed flow reactor	<ul style="list-style-type: none"> <li>Increase in capacity with pore size of silica foam.</li> </ul>	(Yan et al., 2011a)
65 wt% of PEI ( $M_n$ = 423)	Silica foam	4.58	75 °C, 1 atm, 99.99 % CO <sub>2</sub>	Gravimetric	Higher capacity and kinetics than those of 1-D and 2-D based silica materials.	(Wang et al., 2014a)
50 wt% PEI ( $M_n$ = 600)	Immensely disordered silica foam	2.3				

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Table 2 (continued)

PEI	Support	Adsorption capacity (mmol g <sup>-1</sup> )	Conditions	Method	Remarks	Reference
60 % PEI ( $M_n$ = 600)	Pluronic P123 attached silica foam	4.45	25 °C, 1 bar, 99.99 % CO <sub>2</sub> 70 °C, 1 bar, 16.66 % CO <sub>2</sub> /N <sub>2</sub> mixture	Micromeritics ASAP 2020 analyzer Gravimetric	<ul style="list-style-type: none"> <li>Stability in capacity over 10 cycles.</li> <li>Superior selectivity.</li> <li>An enthalpy of adsorption of <math>-85 \text{ kJ mol}^{-1}</math>.</li> </ul>	(Vilarrasa-Garcia et al., 2015) (Yan et al., 2012)
70 % PEI ( $M_n$ = 10000)	Pluronic P123 attached silica foam	3.24	85 °C, 1 atm, 9.64 % CO <sub>2</sub> /H <sub>2</sub> mixture	Fixed-bed reactor connected with GC	–	(Ma et al., 2014)
PEI ( $M_n$ = 10000) + APTMS	Silica foam	2.67	50 °C, 1 atm, 9.64 % CO <sub>2</sub> /H <sub>2</sub> mixture	Fixed-bed reactor connected with GC	Better performance than PEI alone.	(Ma et al., 2014)
50 wt% PEI ( $M_n$ = 25000)	Silica gel	3.14	75 °C, 1 atm, 15 % CO <sub>2</sub> /4.5 % O <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	Higher capacity than SBA-15.	(Zhang et al., 2012)
30 wt% LPEI ( $M_w$ = 423)	Silica gel	2.13	70 °C, 1 atm, 15.1 % CO <sub>2</sub> /N <sub>2</sub> mixture	Packed bed flow reactor	Maintained capacity over 5 adsorption-desorption cycles.	(Wang et al., 2012a)
20 wt% PEI ( $M_w$ = 1300)	Silica gel	4.69	1.85 °C, 34.5 atm, 15 % CO <sub>2</sub> /N <sub>2</sub> mixture	GC connected SS-316 high pressure reactor	Higher capacity than that of APTES.	(Sakpal et al., 2012)
BPEI ( $M_w$ = 600)	Silica gel	2.44	65 °C, 15 % CO <sub>2</sub> /4.5 % O <sub>2</sub> /5.65 % H <sub>2</sub> O/N <sub>2</sub> mixture	Packed bed reactor	Maintained capacity after repeated adsorption-desorption cycles.	(Quang et al., 2016)
60 wt% PEI ( $M_w$ = 600)	Fly ash sourced silica gel	3.30	90 °C, 0.1 bar, 10 % CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	Benefits in terms of adsorption stability, cost effectiveness, and waste management.	(Zhang et al., 2014c)
BPEI ( $M_n$ = 600)	Silica gel	2.2	60 °C, 1 atm, 10 % CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	Maintained capacity after 10 adsorption-desorption cycles.	(Zhao et al., 2013)
25 wt% PEI ( $M_w$ = 800) + 25 wt% diethanolamine	Silica gel	2.93	35 °C, 1 atm, pure CO <sub>2</sub>	Gravimetric	Amine efficiency of 0.40 mol CO <sub>2</sub> /mol N, whereas 0.17 mol CO <sub>2</sub> /mol N along with a capacity of 1.92 mmol g <sup>-1</sup> for neat PEI-silica gel adsorbent.	(Fan et al., 2019)
50 wt% PEI ( $M_w$ = 800)	KIL-2	3.60	90 °C, 1 bar	IMI-HTP manometric sorption analyzer	Lower capacity compared to TEPA - modified KIL-2.	(Ojeda et al., 2017)
PEI ( $M_w$ = 800)	KIT-6	3.00	105 °C, 1 atm, 99.9 % CO <sub>2</sub>	High pressure adsorption setup (iSorbHP1-XKRLSPN100)	–	(Kishor and Ghoshal, 2016)
45 wt% PEI ( $M_n$ = 423)	Silica	3.5	60 °C, 10 % CO <sub>2</sub> /He mixture	Packed bed reactor	–	(Hoffman et al., 2014)
12 wt% PEI ( $M_n$ = 600) + 28 wt% TMPEI ( <i>N</i> -(3-trimethoxysilylpropyl) diethylenediamine)	Silica	1.75	50 °C, 13.4 % CO <sub>2</sub> /4 % He/4 % H <sub>2</sub> O/N <sub>2</sub> mixture	Fixed-bed reactor	Regenerability after 100 more adsorption-desorption cycles.	(Fisher and Gray, 2015)
PEI ( $M_w$ = 800) (PEI to silica weight ratio of 2.76)	Hierarchical bimodal meso-/microporous silica	2.6	50 °C, 1 bar, 400 ppm CO <sub>2</sub> /He mixture	Gravimetric	<ul style="list-style-type: none"> <li>Capacity of 4.1 mmol g<sup>-1</sup> in 10% CO<sub>2</sub>/He mixture at 80 °C.</li> <li>Enhanced CO<sub>2</sub> adsorption performance in the influence of water vapor</li> </ul>	(Kwon et al., 2019)
20 wt% PEI ( $M_w$ = 800)	Hollow fiber of mesoporous silica C803 and poly(amide imide)	1.19	35 °C, 1 atm, 10 % CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	Enhanced capacity with glycerol addition.	(Labreche et al., 2014)
5 wt% APTES + 45 wt% PEI ( $M_n$ = 423)	Silica	3		Packed bed reactor	Good steam stability.	(Hammache et al., 2013)

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Table 2 (continued)

PEI	Support	Adsorption capacity (mmol g <sup>-1</sup> )	Conditions	Method	Remarks	Reference
50 wt% BPEI ( $M_n = 600$ )	Hollow silica microspheres	2.1	60 °C, 1 atm, 5% CO <sub>2</sub> /He mixture	Micromeritics ASAP 2020 analyzer	Regenerability over 5 adsorption-desorption cycles.	(Cecilia et al., 2016)
Epoxide-PEI ( $M_w = 1200$ ) with O/N mole ratio of 0.37	Silica microspheres	2.2	25 °C, 1 atm, 99.9 % CO <sub>2</sub> 40 °C, 15 % CO <sub>2</sub> /3 % H <sub>2</sub> O/2 % Ar/N <sub>2</sub> mixture	Gravimetric -MS	<ul style="list-style-type: none"> <li>• Lower capacity compared to PEI alone.</li> <li>• Stability in capacity.</li> </ul>	(Choi et al., 2016)
50 wt% PEI ( $M_n = 600$ )	TUD-1 mesoporous sponge	2.64	75 °C, 15 % CO <sub>2</sub> /4.5 % O <sub>2</sub> /N <sub>2</sub> mixture	Fixed-bed flow sorption system	<ul style="list-style-type: none"> <li>• Faster adsorption kinetics compared to SBA-15.</li> <li>• Higher capacity in wet condition.</li> </ul>	(Wang et al., 2014c)
60 wt% PEI ( $M_w = 600$ )	Multilamellar silica vesicles	4.73	90 °C, 1 atm, 15 % CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	<ul style="list-style-type: none"> <li>• Faster adsorption kinetics and good cyclic stability.</li> <li>• Increased capacity in wet condition.</li> </ul>	(Zhang et al., 2016b)
25 wt% BPEI ( $M_w = 600$ )	Layered silicate magadiite	1.03	75 °C, 5 % CO <sub>2</sub> /He mixture	Quantachrome CHEMBET-3000 TPD/TPR instrument equipped with a thermocouple detector	<ul style="list-style-type: none"> <li>• Faster desorption kinetics and good thermal stability.</li> <li>• Capacity reduction in the influence of cetyltrimethylammonium ions.</li> </ul>	(Vieira and Pastore, 2014)

Kim et al. (Kim et al., 2019a) through alkylation of PEI-decorated outer surface of macroporous silica by 1,2-epoxybutane, and the resulting generation of tertiary amines. In this system, the tertiary amines serve as reversible adsorbent sites for SO<sub>2</sub>, while CO<sub>2</sub> mainly adsorbs on primary and secondary amines. The resultant CO<sub>2</sub> adsorbent demonstrated only 8.5 % drop from its initial capacity of 3.17 mmol g<sup>-1</sup> (measured at 60 °C) after adsorption/desorption cycles, compared to 65 % drop from its initial capacity of 3.70 mmol g<sup>-1</sup> for typical PEI - impregnated macroporous silica CO<sub>2</sub> adsorbent.

PEI - functionalized hierarchical bimodal meso-/microporous silica was designed by Kwon et al. (Kwon et al., 2019). For an adsorbent with PEI to silica ratio of 2.76, optimal capacities of 2.6 mmol g<sup>-1</sup> in 400 ppm CO<sub>2</sub> at 50 °C, and 4.1 mmol g<sup>-1</sup> in 10 % CO<sub>2</sub> at 80 °C were recorded. In comparison to conventional mesoporous adsorbents, the reported adsorbent displayed an unusual step-like CO<sub>2</sub> adsorption isotherm. The presence of moisture was beneficial. Indeed, an enhanced uptake of 3.36 mmol g<sup>-1</sup> was observed in 400 ppm at 30 °C and 19 % RH.

Development of a CO<sub>2</sub> adsorbent by effective filling of PEI into hollow fiber supports comprising mesoporous silica C803 and poly (amide imide) was reported by Labreche et al. (Labreche et al., 2014). For such system, breakthrough and equilibrium adsorption capacities of ca. 0.85 and 1.19 mmol g<sup>-1</sup>, respectively, were observed at 1 atm and 35 °C using 14 % CO<sub>2</sub>. Interestingly, addition of glycerol into the above composition was favorable to further enhance adsorption capacity.

Hammache et al. (Hammache et al., 2013) reported that the infusion of APTES into silica - supported PEI enhanced the capture efficiency and the steam stability. Under atmospheric pressure and 60 °C, an adsorption capacity of ca. 3 mmol g<sup>-1</sup> was acquired for such sorbent. In another work, Fauth et al. (Fauth et al., 2012) examined the combinatorial impact of PEI and APTES on the CO<sub>2</sub> capture of mesoporous silica. An increased amine efficiency was implied for such sorbents due to the facilitated CO<sub>2</sub> diffusion into PEI, yet the observed CO<sub>2</sub> uptake was lower for such adsorbent as compared to pure PEI - loaded silica.

Cecilia et al. (Cecilia et al., 2016) prepared PEI supported by silica hollow microspheres resulting in a CO<sub>2</sub> uptake of 2.1 mmol g<sup>-1</sup> at 25 °C and 760 mmHg for an adsorbent corresponding to 50 wt% BPEI ( $M_n = 600$ ). The regenerability of such adsorbent was confirmed by executing 5 consecutive cycles of operation. Choi et al. (Choi et al., 2016) developed epoxide-PEI and used it for the modification of 3-dimensional silica microspheres acquiring an adsorbent exhibiting both good capacity and stability. Specifically, an adsorption capacity of ca. 2.2 mmol g<sup>-1</sup> at 40 °C in a flue gas containing 15 % CO<sub>2</sub> was achieved, together with good cyclic stability upon desorption at 120 °C. However, when compared to neat PEI - modified system, the observed adsorption capacity of the epoxide-PEI - modified system was lower.

Wang et al. (Wang et al., 2014c) reported the generation of CO<sub>2</sub> adsorbents based on PEI - impregnated TUD-1 mesoporous sponge. For 50 wt% PEI - impregnated TUD-1, maximum adsorption capacities of ca. 2.64 and 2.96 mmol g<sup>-1</sup> were acquired at atmospheric pressure and 75 °C in dry and wet conditions, respectively. In addition, these systems exhibited faster adsorption kinetics in comparison to the analogous SBA-15 based system, as well as appreciable figures in terms of cyclic and thermal stability.

Zhang et al. (Zhang et al., 2016b) used multilamellar silica vesicles possessing mesoporous structure to support PEI for CO<sub>2</sub> capture. The introduced PEI was observed to disperse well in the mesoporous silica vesicles due to the combined influence of remaining surfactant and multilamellar mesoporous network. As a result, a strongly enhanced CO<sub>2</sub> adsorption capacity of 4.73 mmol g<sup>-1</sup> was obtained in dry CO<sub>2</sub> at 90 °C, which was further enhanced in wet conditions. Moreover, this system demonstrated fast adsorption kinetics and good cyclic stability.

Vieira et al. (Vieira and Pastore, 2014) prepared silicate magadiite possessing layered structure and then functionalized it using BPEI ( $M_w = 600$ ). Therein, the highest adsorption capacity of 1.03 mmol g<sup>-1</sup>

Table 3

Summarized adsorption properties for CO<sub>2</sub> sorbents based on various clay and carbonaceous materials - supported polyethylenimines (PEI: polyethylenimine; LPEI: linear polyethylenimine; BPEI: branched polyethylenimine; GO: graphene oxide; CNTs: carbon nanotubes; SWCNTs: single-walled carbon nanotubes; MWCNTs: multi-walled carbon nanotubes; GC: gas chromatography).

PEI	Support	Adsorption capacity (mmol g <sup>-1</sup> )	Conditions	Method	Remarks	Reference
50 wt% BPEI ( $M_n = 600$ )	6 M HCl - treated MMT	2.55	75 °C, 1 atm, 99.99 % CO <sub>2</sub>	Gravimetric	<ul style="list-style-type: none"> <li>Higher capacity in 3% moisture.</li> <li>Capacity of 2.51 mmol g<sup>-1</sup> in 15% CO<sub>2</sub>/N<sub>2</sub> mixture.</li> <li>Appreciable recycling and thermal stabilities.</li> <li>Superior performance than kaolinite - based system.</li> </ul>	(Wang et al., 2014b)
37 wt% PEI	Palygorskite	1.53	45 °C, 1 bar, pure CO <sub>2</sub>	VTI	Capacity of 1.52, 1.38, 1.27, and 1.04 mmol g <sup>-1</sup> , for respective saponite, MMT, sepiolite, and bentonite - based adsorbents.	(Gómez-Pozuelo et al., 2019)
30 wt% BPEI ( $M_n = 600$ )	HNO <sub>3</sub> - treated sepiolite	1.70	65 °C, 1 bar, 99.99 % CO <sub>2</sub>	Scientific Instruments HVPDA-100 equipment	CO <sub>2</sub> /N <sub>2</sub> selectivity of 440 mol CO <sub>2</sub> /mol N <sub>2</sub> .	(Vilarasa-García et al., 2017b)
50 wt% PEI ( $M_w = 600$ )	HCl - treated sepiolite clay fibers	2.48	75 °C, 1 atm, 60 % CO <sub>2</sub> /N <sub>2</sub> mixture	Magnetic suspension balance (Rubotherm)	Maintained 98 % of capacity after 10 adsorption-desorption cycles.	(Ouyang et al., 2018)
35 wt% PEI ( $M_w = 17000$ )	Purified halloysite nanotubes	1.25	25 °C, dry air	Gravimetric	Regenerability after 50 cycles.	(Cai et al., 2015)
50 wt% BPEI ( $M_w = 800$ )	Calcined + HCl - treated halloysite nanotubes	2.75	85 °C, 0.6 bar, 60 % CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	Superior regenerability.	(Niu et al., 2016)
30 wt% PEI ( $M_n = 800$ )	HNTs derived silica mesoporous nanotubes	7.84	20 °C, 9 bar, pure CO <sub>2</sub>	An adsorption setup	Only 5 % drop in capacity after 15 adsorption-desorption cycles.	(Taheri et al., 2019)
30 wt% LPEI ( $M_w = 600$ )	Bentonite	1.07	75 °C, 1 bar, 99.99 % CO <sub>2</sub>	Gravimetric	<ul style="list-style-type: none"> <li>Capacity of only 0.14 mmol g<sup>-1</sup> for neat bentonite.</li> <li>Benefits in terms of CO<sub>2</sub>/N<sub>2</sub> selectivity and regenerability.</li> </ul>	(Chen et al., 2013a)
60 wt% BPEI ( $M_n = 600$ )	Bentonite porous heterostructures	1.47	25 °C, 1 bar	Micromeritics ASAP 2020 Analyzer	-	(Vilarasa-García et al., 2017a)
60 wt% BPEI ( $M_w = 25000$ )	HNO <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub> - treated GO	0.75	25 °C, 1 atm, 15 % CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	CO <sub>2</sub> /N <sub>2</sub> selectivity of 37.13.	(Shin et al., 2016)
PEI ( $M_w = 800$ ) (PEI to GO weight ratio of 3)	NaOH - incorporated GO	2.5	-0.15 °C, 1.05 bar	Micromeritics TriStar II 3020 analyzer	-	(Sui et al., 2013)
PEI ( $M_w = 600$ ) (PEI to GO weight ratio of 3.3)	GO particles	2.91	75 °C, 99.99 % CO <sub>2</sub>	Gravimetric	Only 8.9 % drop in capacity after 8 adsorption-desorption cycles.	(He et al., 2019)
<i>In situ</i> polymerized PEI (aziridine to hydroxylated graphene weight ratio was 1.98)	Hydroxylated graphene	4.13	25 °C, 1 atm, 10 % CO <sub>2</sub> /Ar mixture	Gravimetric	-	(Liu et al., 2015a)
60 wt% of PEI ( $M_n = 600$ )	Graphene/silica hybrid	3.89	75 °C, 1 bar, 15 % CO <sub>2</sub> /N <sub>2</sub> mixture	Magnetic suspension microbalance (Rubotherm) connected with GC	Maintained capacity after 20 cycles.	(Yang et al., 2013)
25 wt% PEI ( $M_w = 600$ )	Graphene/γ-alumina nanorods hybrid	1.14	75 °C, 1 atm, 15 % CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	Reduced PEI degradation tendency by cause of thermal transfer capability.	(Bhowmik et al., 2016)
20 wt% PEI ( $M_w = 800$ )	MWCNTs	2.12	30 °C, 1 atm, 0.15 % CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	10 % reduction in capacity after 10 cycles.	(Keller et al., 2018)
BPEI ( $M_w = 25000$ )	SWCNTs	2.1	25 °C, 1 atm, 99.99 % CO <sub>2</sub>	Gravimetric	Higher capacity than that of MWCNTs.	(Dillon et al., 2015)
PEI ( $M_w = 750000$ )	HNO <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub> - treated MWCNTs	2.14	25 °C, 1 bar, 99.99 % CO <sub>2</sub>	Gravimetric	<ul style="list-style-type: none"> <li>Capacity of 0.34 mmol g<sup>-1</sup> at 40 °C using 15 % CO<sub>2</sub>/N<sub>2</sub> mixture.</li> <li>Good stability over 10 cycles.</li> </ul>	(Lee et al., 2015b)
BPEI ( $M_w = 1300$ g mol <sup>-1</sup> ) + purine (spacer molecule)	MWCNTs	3.875	50 °C, 1 bar, pure CO <sub>2</sub>	Gravimetric	<ul style="list-style-type: none"> <li>Other benefits such as low heat of adsorption (29 kJ mol<sup>-1</sup>), appreciable stability over 50 adsorption-desorption cycles and fast kinetics.</li> <li>Capacity of only 0.6520 mmol g<sup>-1</sup> for neat PEI-MWCNTs.</li> </ul>	(Deng and Park, 2019)

(continued on next page)

Table 3 (continued)

PEI	Support	Adsorption capacity (mmol g <sup>-1</sup> )	Conditions	Method	Remarks	Reference
15 wt% BPEI ( $M_w = 25000$ )	CNTs/activated carbon fiber hybrid	2.25	30 °C, 1 atm, 99.99 % CO <sub>2</sub>	Gravimetric	<ul style="list-style-type: none"> <li>● Increase in capacity with temperature up to 60 °C.</li> <li>● Maintained 96 % more capacity after cyclic operations.</li> </ul>	(Kong et al., 2013)
40 wt% PEI with ethylenediamine end-capping ( $M_n = 600$ )	MWCNTs	2.54	69.85 °C, 1 atm, 10 % CO <sub>2</sub> /N <sub>2</sub> mixture	Adsorption column connected with GC	Complete regeneration at temperature > 403 K.	(Liu et al., 2014)
PEI ( $M_w = 25000$ ) (loading amount was 5 fold greater than buckminsterfullerene)	Buckminsterfullerene	3.19	90 °C, 0.1 bar, 99.99 % CO <sub>2</sub>	Gravimetric	<ul style="list-style-type: none"> <li>● Superior resistance towards methane absorption.</li> <li>● 2 fold higher capacity than that of Mg-MOF-74.</li> </ul>	(Andreoli et al., 2014)
70 wt% BPEI ( $M_w = 600$ )	Activated carbon	2.55	28 °C, 1 atm, 15 % CO <sub>2</sub> /N <sub>2</sub> mixture	Fixed-bed flow sorption system equipped with GC	Increase in capacity under the influence of moisture.	(Pino et al., 2016)
65 wt% PEI ( $M_w = 600$ )	Mesoporous carbon	4.82	75 °C, 1 atm, 15 % CO <sub>2</sub> /N <sub>2</sub> mixture	Fixed-bed flow adsorber connected to GC	<ul style="list-style-type: none"> <li>● Only 4 % reduction in capacity after 10 cycles.</li> <li>● Increase in capacity under the influence of moisture.</li> </ul>	(Wang et al., 2013a)
55 wt% BPEI ( $M_w = 600$ ) + 5 wt% Span 80 (nontoxic surfactant)	Mesoporous carbon	2.25	25 °C, 400 ppm CO <sub>2</sub> /N <sub>2</sub> mixture	Fixed-bed flow adsorber connected to GC	<ul style="list-style-type: none"> <li>● Better capacity than those of 55 and 60 wt% PEI.</li> <li>● Capacity of 3.34 mmol g<sup>-1</sup> in 5000 ppm CO<sub>2</sub>.</li> </ul>	(Wang et al., 2015a)
39 wt% <i>in situ</i> polymerized PEI	Mesoporous carbon	3.13	30 °C, 1 atm, 99.99 % CO <sub>2</sub>	Gravimetric	Capacity of 3.52 mmol g <sup>-1</sup> for 37 wt% <i>in situ</i> polymerized polyvinylamine - modified mesoporous carbon (ca. 2 fold higher than that of neat mesoporous carbon)	(Hwang et al., 2011)
PEI ( $M_w = 600$ ) (same loading amount as that of support)	Nanoporous carbon	1.09	75 °C, 30 % CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	–	(Tang et al., 2013)
50 wt% PEI + 25 wt% K <sub>2</sub> CO <sub>3</sub>	Activated carbon	3.6	60 °C, 8 % CO <sub>2</sub> /10 % H <sub>2</sub> O/N <sub>2</sub> mixture	Fixed-bed reactor system	–	(Guo et al., 2014)
PEI ( $M_n = 1200$ )	Carbon sphere	3.39	75 °C, 1 atm, 99.99 % CO <sub>2</sub>	Gravimetric	<ul style="list-style-type: none"> <li>● 25.7 % increase in capacity after the infusion of 20 wt% PEG (<math>M_w = 6000</math>).</li> <li>● Lower cyclic stability than that of PEI (<math>M_n = 10000</math>) - based system.</li> </ul>	(Wang et al., 2016a)
45 wt% PEI ( $M_w = 800$ )	Carbon nanosphere	1.97	75 °C, 1 bar, 99.99 % CO <sub>2</sub>	Gravimetric	Higher capacity than that of carbon microsphere - based system.	(Chai et al., 2016)

at 75 °C was achieved for the adsorbent loaded with 25 wt% BPEI, also exhibiting fast desorption kinetics and good thermal reliability. Though, the influence of cetyltrimethylammonium ions negatively affected the adsorption capacity of such adsorbent due to the reduction in inner sites adsorption.

## 2.2. Clay – supported PEI

Clay based materials have attracted attention for CO<sub>2</sub> capture applications due to their potential to overcome issues related to commercial availability, cost, and hydrothermal stability (Wang et al., 2013b, b). Clays are cost effective materials that are available abundantly in nature having a molecular structure that comprises a combinatorial sheet of tetrahedral silicates and octahedral hydroxides. These characteristics together with appreciable chemical and mechanical stability make clays appropriate as support materials for CO<sub>2</sub> capture (Jozefaciuk and Bowanko, 2002; Karahan et al., 2006; Roth et al., 2013), though acid or alkaline treatment is often necessary in order to overcome deficiencies related to textural features, which may compromise their application potential (Jozefaciuk and Matyka-Sarzynska, 2006; Wang et al., 2014b). This section examines works on various clay - supported PEI sorbent systems based on montmorillonite, kaolinite, sepiolite, saponite, palygorskite, halloysite, and bentonite.

Formation of BPEI - impregnated clays for CO<sub>2</sub> adsorption was reported by Wang et al. (Wang et al., 2014b). The clays were pretreated with either acid or alkali in order to increase surface area and pore volume, and thereby to enhance BPEI impregnation efficiency. The authors examined the suitability of two types of clays, i.e., kaolinite and montmorillonite (MMT). In comparison to other studied systems, MMT treated with 6 M HCl exhibited significantly enhanced surface area and porosity. At 75 °C, the observed CO<sub>2</sub> adsorption capacities for MMT with 50 wt% PEI loading were ca. 2.55 mmol g<sup>-1</sup> and 3.23 mmol g<sup>-1</sup> in dry conditions and at 3% moisture, respectively, coupled also to appreciable cycling and thermal stabilities. Gomez-Pozuelo et al. (Gómez-Pozuelo et al., 2019) developed a series of PEI - impregnated clays, and CO<sub>2</sub> capacities of 1.53, 1.52, 1.38, 1.27, and 1.04 mmol g<sup>-1</sup> were recorded at 45 °C and 1 bar into palygorskite, saponite, MMT, sepiolite, and bentonite, respectively, after 37 wt% PEI loading.

Vilarrasa-Garcia et al. (Vilarrasa-García et al., 2017b) designed a solid CO<sub>2</sub> sorbent based on sepiolite by following initial microwave radiation aided by HNO<sub>3</sub> treatment and subsequent PEI impregnation. For such an adsorbent with 30 wt% of BPEI ( $M_n = 600$ ), a CO<sub>2</sub> uptake of ca. 1.70 mmol g<sup>-1</sup> was observed at 1 atm and 65 °C. Additionally, high CO<sub>2</sub>/N<sub>2</sub> selectivity value of ca. 440 mol CO<sub>2</sub>/mol N<sub>2</sub> was achieved. Ouyang et al. (Ouyang et al., 2018) presented the fabrication of CO<sub>2</sub> adsorbent through the PEI loading into HCl - treated sepiolite clay fibers. Acid treatment of sepiolite clay resulted in the generation of MgO-SiO<sub>2</sub> nanowires. The obtained CO<sub>2</sub> adsorption capacity at 75 °C and 1 atm was 2.48 mmol g<sup>-1</sup> for PEI loading of 50 wt%. This system maintained ca. 98 % of its adsorption capacity after 10 successive adsorption-desorption cycles.

Cai et al. (Cai et al., 2015) reported the functionalization of halloysite nanotubes (HNTs) by PEI impregnation for CO<sub>2</sub> capture. Adsorption studies at room temperature (25 °C) revealed a capacity of 1.25 mmol g<sup>-1</sup> for 35 wt% PEI loading, with appreciable regenerability for over 50 cycles. In another work, Niu et al. (Niu et al., 2016) reported a nanocomposite adsorbent designed by impregnating PEI into pretreated HNTs for CO<sub>2</sub> capture. HNTs pre-treatment, which included calcination and subsequent HCl treatment, resulted in generation of silica mesoporous nanotubes with enhanced specific surface area and pore volume. After PEI impregnation, this material displayed an adsorption uptake of ca. 2.75 mmol g<sup>-1</sup> at 85 °C for 50 wt% PEI. Also, cyclic analysis underlined the promising regenerability for this adsorbent. An uptake of 7.84 mmol g<sup>-1</sup> was reported by Taheri et al. (Taheri et al., 2019) at 9 bar and 20 °C for a nanocomposite adsorbent consisting of 30 wt% PEI ( $M_n = 800$ ) - modified silica mesoporous

nanotubes. Notably, the drop in adsorption performance was limited to only 5 % after 15 adsorption-desorption cycles.

A PEI/bentonite composite adsorbent was prepared by Chen et al. (Chen et al., 2013a). Analysis at 75 °C and 1 bar revealed an adsorption capacity of ca. 1.07 mmol g<sup>-1</sup> after the infusion of 30 wt% of PEI, versus ca. 0.14 mmol g<sup>-1</sup> for the neat bentonite, with promising CO<sub>2</sub>/N<sub>2</sub> selectivity and regenerability. In another study, Vilarrasa-Garcia et al. (Vilarrasa-García et al., 2017a) reported the preparation of porous heterostructures from bentonite and then carried out PEI functionalization for CO<sub>2</sub> capture application, where PEI contributed to capture CO<sub>2</sub> by chemical means through the reaction of the amine groups with CO<sub>2</sub>. Analysis at 25 °C and 1 bar unveiled an adsorption capacity of 1.47 mmol g<sup>-1</sup> for 60 wt% of BPEI loading ( $M_n = 600$ ). Table 3 provides summarized adsorption performance data for the various clay - supported PEI CO<sub>2</sub> sorbents.

Among the clay - supported PEI CO<sub>2</sub> sorbents, a notable capacity at low pressure (0.6 bar) of 2.75 mmol g<sup>-1</sup> (Niu et al., 2016) is highlighted for combined calcined and HCl-treated halloysite based system. At the same time, the performance with respect to capture capacity of clay-supported PEI sorbents is observed to be lower than the conventional silica based systems, whereas higher in terms of regenerability. Additional efforts have to be generated for effective tuning of textural features of clay materials and subsequent PEI attachment.

## 2.3. Carbonaceous materials with PEI

Carbonaceous materials are widely used for CO<sub>2</sub> capture applications in account of their advantageous features that include high specific surface area, tunable porosity, flexibility in surface modification, superior chemical and thermal stability, appreciable mechanical features, availability in various forms, and cost-effectiveness originating mainly from the low cost of the raw materials used to produce carbonaceous adsorbents (Arenillas et al., 2005; Iqbal et al., 2017; Kueh et al., 2018; Samanta et al., 2011). This section deals with various carbonaceous materials such as graphene oxide/graphene, activated carbon, carbon spheres, carbon nanotubes, and fullerenes, used as PEI supports to yield CO<sub>2</sub> sorbent systems. A summary of the adsorption properties for the various PEI - loaded carbonaceous CO<sub>2</sub> sorbents is presented in Table 3.

### 2.3.1. Graphene oxide/graphene – supported PEI

Graphene oxide (GO) is one of the major graphene-based products with a graphite atomic sheet structure composed of sp<sup>2</sup> and sp<sup>3</sup> hybridized carbons holding various surface oxygen functionalities like carboxyl, carbonyl, hydroxyl, and epoxy (Eng et al., 2017; Krishnamoorthy et al., 2013; Marciano et al., 2010; Pokhrel et al., 2018a; Varghese et al., 2020). The porosity of the material lies on the few-layer, intercalated/exfoliated forms as well in the interconnectivity of the graphene flakes upon growth, which leave a porous configuration to the final material. Due to the availability of the functional groups on the surface, GO can be successfully functionalized with other moieties by chemical means and be thereby tuned for targeted sorption applications. In addition, the influence of the layered morphology and associated porous nature opens up numerous perspectives for CO<sub>2</sub> capture (Balasubramanian and Chowdhury, 2015; Nováček et al., 2017; Varghese et al., 2020). Fig. 5 demonstrates the mechanism of interactions upon PEI functionalization of graphene oxide.

Preparation of CO<sub>2</sub> sorbents based on PEI - impregnated GO was reported by Shin et al. (Shin et al., 2016). The authors carried out acid pretreatment of GO using combination of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> to introduce more carboxyl and hydroxyl moieties, and thus enhance PEI loading. The influence of BPEI ( $M_w = 25,000$ ) on GO yielded higher CO<sub>2</sub> capacity and selectivity due to the interaction of the amine moieties with CO<sub>2</sub>. Specifically, the adsorption capacity of the studied samples was increased with increase in BPEI amount up to 60 wt%, and a capacity of ca. 0.75 mmol g<sup>-1</sup> was noted down at 1 atm and 298 K. This system



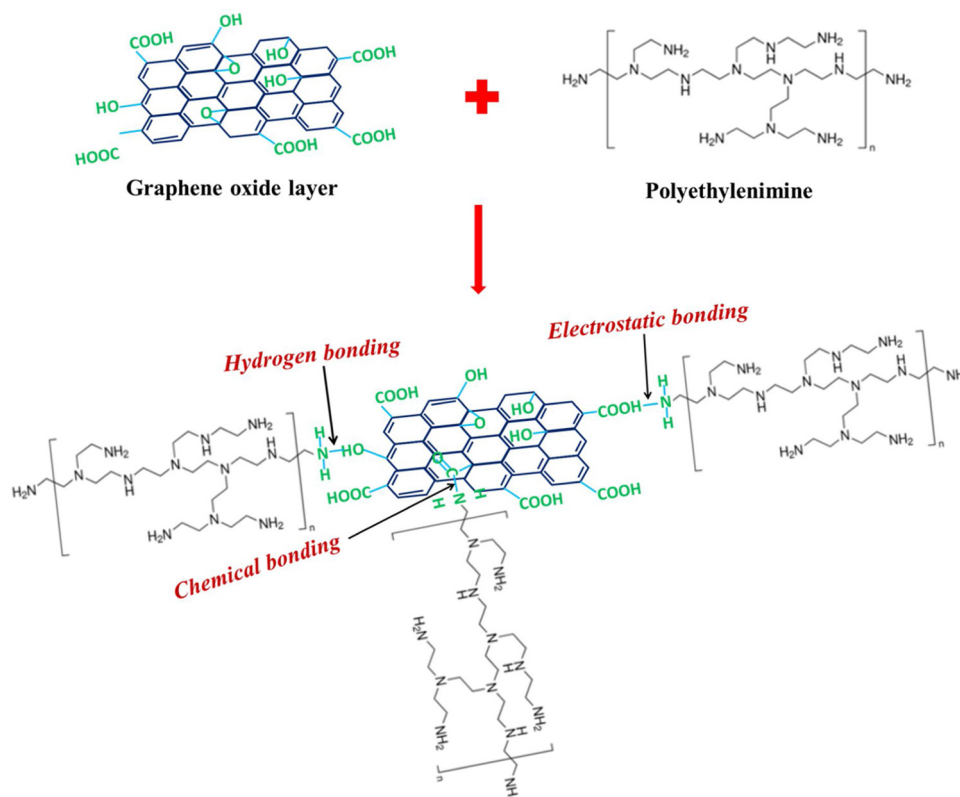


Fig. 5. Schematic representation of PEI functionalization of graphene oxide.

displayed a  $\text{CO}_2/\text{N}_2$  selectivity of 37.13. In another work, Sui et al. (Sui et al., 2013) developed lightweight 3-dimensional porous adsorbent materials comprising of GO and PEI possessing large surface area. In this study, the authors prepared GO-PEI hydrogel by mixing aqueous PEI solution into NaOH incorporated aqueous GO dispersion, followed by 24 h vacuum freeze-drying after the removal of NaOH and unreacted PEI from the hydrogel using high-purity water. At 273 K and 1 bar, this 3-dimensional porous  $\text{CO}_2$  adsorbent with PEI to GO weight ratio of 3 displayed an adsorption capacity of ca.  $2.5 \text{ mmol g}^{-1}$ . He et al. (He et al., 2019) reported a  $\text{CO}_2$  adsorption capacity of  $2.91 \text{ mmol g}^{-1}$  for GO - immobilized PEI at  $75^\circ\text{C}$ , while the recorded drop in performance after 8 adsorption-desorption cycles was 8.9 %.

Non-oxidized graphene (i.e. as grown or reduced), a 2-dimensional  $\text{sp}^2$  hybridized carbon analogue with honeycomb like arrangement (Geim and Novoselov, 2010; Varghese and Mittal, 2019; Varghese et al., 2018), also displays promise for capture of  $\text{CO}_2$  (Balasubramanian and Chowdhury, 2015; Najafabadi, 2015; Nováček et al., 2017). Research conducted by Liu et al. (Liu et al., 2015a) revealed a high  $\text{CO}_2$  uptake for an adsorbent developed through grafting of PEI into hydroxylated version of 3-dimensional graphene. Adsorption analysis conducted at  $25^\circ\text{C}$  and 1 atm showed a  $\text{CO}_2$  uptake of ca.  $4.13 \text{ mmol g}^{-1}$  for such adsorbent with aziridine to graphene mass ratio of 1.98. This system also displayed good regenerability due to the PEI - based interaction on the hydroxylated graphene surface.

A  $\text{CO}_2$  sorbent resulted by impregnation of PEI into graphene-silica hybrid sheets was reported by Yang et al. (Yang et al., 2013). By virtue of the large number of  $\text{CO}_2$ -philic amine groups, thin layered morphology, and good thermal conductivity, the resultant  $\text{CO}_2$  sorbent exhibited more efficient thermal transfer and beneficial  $\text{CO}_2$  adsorption and regeneration characteristics. Accordingly, the composite adsorbent composed of 12 wt% graphene and 60 wt% PEI showed an adsorption capacity of ca.  $3.89 \text{ mmol g}^{-1}$  at  $75^\circ\text{C}$  and 100 kPa. In addition, the adsorption capacity of this adsorbent remained almost unaltered after 20 repeated  $\text{CO}_2$  adsorption-desorption cycles.

A hybrid  $\text{CO}_2$  adsorbent comprising PEI - functionalized graphene/ $\gamma$ -alumina nanorods hybrid was reported by Bhowmik et al. (Bhowmik et al., 2016). The influence of graphene in the formulation of such adsorbent was found to enhance the surface area and thermal conductivity. To this end, the resultant adsorbent system showed faster thermal transfer capability and reduced PEI degradation tendency. A  $\text{CO}_2$  adsorption capacity of ca.  $1.14 \text{ mmol g}^{-1}$  was noted at  $75^\circ\text{C}$  and 1 atm, for the 25 wt% PEI - impregnated  $\gamma$ -alumina nanorods/graphene hybrid. In addition, efficient adsorption-desorption cyclic operation was established at  $75^\circ\text{C}$  and  $100^\circ\text{C}$ , respectively.

### 2.3.2. Carbon nanotube – supported PEI

Since their introduction in 1991 by Iijima et al. (Iijima, 1991), carbon nanotubes (CNTs), roll-up analogues of graphene with nanoscale diameter in single- as well as multiple walled forms, have received considerable attention for separation applications owing to their high surface area, large aspect ratio, availability of multiple adsorption sites, light weight, flexibility, superior mechanical characteristics, chemical stability, and modification capability (Ajayan and Zhou, 2001; Su et al., 2009; Vengatesan et al., 2017; Zhao et al., 2002; Vermisoglou et al., 2010; Pilatos et al., 2010). For  $\text{CO}_2$  capture, CNT - supported amine systems have attracted interest because of their thermo-mechanical properties, unique physicochemical features, chemical stability, and more (Iqbal et al., 2017; Niu et al., 2015; Su et al., 2014). However, high production cost and sorbent fabrication difficulties need to be overcome in order for such systems to deploy their full potential for practical  $\text{CO}_2$  capture applications (Iqbal et al., 2017, 2016).

Preparation of PEI - filled multiwall carbon nanotubes (MWCNTs) as  $\text{CO}_2$  adsorbents using wet impregnation in ethanol was reported Keller et al. (Keller et al., 2018). Out of various compositions studied, 20 wt% PEI - filled MWCNTs displayed the highest  $\text{CO}_2$  adsorption capacity at ambient pressure and  $30^\circ\text{C}$ , namely  $2.12 \text{ mmol g}^{-1}$  for 15 %  $\text{CO}_2$ . After 10 successive adsorption-desorption cycles, a reduction of about 10 % in adsorption capacity was observed. In another work, Dillon et al.

(Dillon et al., 2015) reported that a CO<sub>2</sub> adsorption capacity of 2.1 mmol g<sup>-1</sup> at 25 °C and 1 atm for BPEI - loaded single-walled carbon nanotubes (SWCNTs), which was higher compared to that of BPEI - loaded MWCNTs.

Lee et al. (Lee et al., 2015b) examined acid pre-treatment of MWCNTs using a combination of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> before PEI impregnation to obtain more carboxyl groups and also to release metal based surface contaminants. The adsorption capacity of MWCNTs was observed to increase after the impregnation of PEI resulting in a capacity of ca. 2.14 mmol g<sup>-1</sup> at 1 bar and 298 K for simulated flue gas containing 15 % CO<sub>2</sub>. In addition, repeated cyclic operations had no significant impact on the adsorption capacity of this adsorbent. Deng et al. (Deng and Park, 2019) revealed the applicability of spacer molecules, i.e., purine, to enhance adsorption performance of PEI - decorated MWCNTs. Accordingly, a capacity of 3.9 mmol g<sup>-1</sup> was reported at 50 °C and 1 bar, while the respective value for neat PEI-MWCNTs was only 0.7 mmol g<sup>-1</sup>. Other benefits such as low heat of adsorption (29 kJ mol<sup>-1</sup>), appreciable stability over 50 adsorption-desorption cycles, and enhanced kinetics are also to be highlighted. Infusion of BPEI ( $M_w = 25,000$ ) into composite structure composed of CNTs and activated carbon fibers was reported by Kong et al. (Kong et al., 2013). BPEI enhanced the CO<sub>2</sub> adsorption capacity of the composite adsorbent from 1.51 to 2.25 mmol g<sup>-1</sup> at 30 °C and 1 atm, which was observed to further increase with increase in temperature up to 60 °C. For this system, a regenerability efficiency of more than 96 % was obtained after repeated cyclic operations. PEI holding ethylenediamine end capping (PEI-ED) was used by Liu et al. (Liu et al., 2014) for functionalization of MWCNTs, and the CO<sub>2</sub> adsorption performance of the resulting adsorbent was compared to that of MWCNTs - supported BPEI. Adsorption analysis at 70 °C and 1 atm disclosed that the highest CO<sub>2</sub> uptake capacity of ca. 2.54 mmol g<sup>-1</sup> was obtained for 40 wt% PEI-ED - loaded MWCNTs. Also, complete regeneration was achieved at temperature above 130 °C. A hollow fiber CO<sub>2</sub> adsorbent comprising of BPEI ( $M_w = 800$ ) - filled MWCNTs/silica was developed by Keller et al. (Keller et al., 2019). A capacity of 1.92 mmol g<sup>-1</sup> was recorded at 30 °C and 0.15 bar for such an adsorbent consisting of 70 wt% silica and 20 wt % BPEI.

### 2.3.3. Fullerene – supported PEI

Fullerenes, 0-dimensional wraps of carbon atoms in the form of hollow spheres, have also been reported for CO<sub>2</sub> capture applications due to unique features such as surface area, spherical shape, monodispersity, thermomechanical properties, tailorable physicochemical characteristics, and functionalization flexibility (De Silva et al., 2014; Gao et al., 2011; Geim and Novoselov, 2010). On the basis of our investigation, we review available works related to fullerene-PEI based CO<sub>2</sub> sorbent systems in this section.

Buckminsterfullerene (C<sub>60</sub>) crosslinked PEI adsorbents exhibiting good capture capacity together with high selectivity were prepared by Andreoli et al. (Andreoli et al., 2014). Accordingly, at 90 °C and 0.1 bar, a CO<sub>2</sub> uptake capacity of 3.19 mmol g<sup>-1</sup> was obtained. The developed CO<sub>2</sub> adsorbents showed also high selectivity against methane, indicating potential in natural gas sweetening applications. In another attempt, the authors examined the effect of pyrolysis in inert atmosphere (argon) on the CO<sub>2</sub> performance of C<sub>60</sub> - supported PEI. A higher CO<sub>2</sub> capture capacity of 2.73 mmol g<sup>-1</sup> was discerned at 25 °C as compared to one observed at 90 °C. A reduction trend in capture capacity at 90 °C after pyrolysis at differing temperatures is related to the molecular scission of C-N backbone associated to PEI in the composite system (Andreoli and Barron, 2015).

### 2.3.4. Activated carbon – supported PEI

Activated carbon, or activated charcoal, is one of the widely reported carbonaceous materials for CO<sub>2</sub> capture applications by account of its large specific surface area with typically small sized pores, low regeneration energy, hydrophobicity, wide availability of sources to

grow these materials, and cost effectiveness (Drage et al., 2009; Pevida et al., 2008b; Plaza et al., 2010; Sethia and Sayari, 2015). In order to enhance CO<sub>2</sub> performance, various attempts on surface functionalization have been reported. In this section, we discuss the studies related to PEI - functionalized activated carbon based CO<sub>2</sub> sorbent systems.

PEI functionalization of activated carbon was found to yield enhanced CO<sub>2</sub> adsorption performance as temperature increases (Choi and Lee, 2015). Indicatively, an adsorption capacity of ca. 1.31 mmol g<sup>-1</sup> was observed at 100 °C for 10 wt% PEI loading. Pino et al. (Pino et al., 2016) also prepared PEI - loaded activated carbon adsorbents and reported a dynamic capacity of ca. 2.55 mmol g<sup>-1</sup> at 28 °C and atmospheric pressure in 15 % CO<sub>2</sub> for 70 wt% PEI loading.

PEI impregnation into mesoporous carbon was reported by Wang et al. (Wang et al., 2013a). Among the various compositions studied, the 65 wt% PEI system displayed optimum CO<sub>2</sub> capacity of ca. 4.82 mmol g<sup>-1</sup> at 75 °C and 1 atm in a CO<sub>2</sub> concentration of 15 %, which is attributed to the high amine content and internal mass-transfer effects. In addition, the influence of moisture was found to be positive in the adsorption capacity of this material, which also exhibited appreciable stability and regenerability. In another study, the authors examined the effectiveness of such sorbent material in low CO<sub>2</sub> concentrations. Accordingly, in 5000 and 400 ppm CO<sub>2</sub>, adsorption capacities of ca. 3.34 and 2.25 mmol g<sup>-1</sup> at 25 °C, respectively, were obtained for mesoporous carbon - modified with 55 wt% PEI and 5 wt% of the nonionic surfactant, Span 80 (Wang et al., 2015a).

Fabrication of CO<sub>2</sub> adsorbent using mesoporous carbon - supported PEI by *in situ* synthesis was reported by Hwang et al. (Hwang et al., 2011). A sorbent with 39 wt% of PEI showed an optimal CO<sub>2</sub> capture capacity of ca. 3.13 mmol g<sup>-1</sup>, as revealed by gravimetric analysis at 1 atm and 30 °C using 10 % CO<sub>2</sub>. A nanoporous carbon/PEI composite was developed by Tang et al. (Tang et al., 2013), which exhibited an adsorption capacity of 1.09 mmol g<sup>-1</sup> at 75 °C when equal mass of PEI and nanoporous carbon was used. A 3-D hybrid CO<sub>2</sub> adsorbent consisting of 40 wt% PEI - impregnated porous carbon, which mimics the layered structure of graphene, was prepared by Shen et al. (Shen et al., 2019). A capacity of 2.66 mmol g<sup>-1</sup> was obtained at 75 °C and ambient pressure. This capacity was retained for up to 12 repeated cycles of adsorption/desorption.

Guo et al. (Guo et al., 2014) studied the CO<sub>2</sub> adsorption behavior of activated carbon after combined impregnation with PEI and K<sub>2</sub>CO<sub>3</sub>, and also compared its performance with the individually loaded systems. After incorporation with 50 wt% PEI/K<sub>2</sub>CO<sub>3</sub>, a higher CO<sub>2</sub> adsorption capacity was obtained, i.e. 3.6 mmol g<sup>-1</sup> at 60 °C using a mixture of 8 % CO<sub>2</sub>/10 % H<sub>2</sub>O, compared to PEI or K<sub>2</sub>CO<sub>3</sub> individually loaded systems. The combinatorial effect of PEI and K<sub>2</sub>CO<sub>3</sub> was also shown to offer good regenerability upon repeated adsorption-desorption cycles.

### 2.3.5. Carbon spheres – supported PEI

Carbon spheres, another technologically versatile and promising class of carbonaceous materials, are also reported for CO<sub>2</sub> capture applications owing to features such as high specific surface area, small sized pores, large porosity, shape and curvature (Deshmukh et al., 2010; Liu et al., 2012a; Wickramaratne and Jaroniec, 2013; Wickramaratne et al., 2014). The reported studies related to CO<sub>2</sub> sorbent systems based on carbon sphere - supported PEI are summarized below.

Mesoporous carbon sphere - supported PEI CO<sub>2</sub> sorbents were developed and studied by Wang et al. (Wang et al., 2016a). Among the different molecular weights used, PEI with  $M_n$  of 1200 displayed the highest CO<sub>2</sub> uptake (ca. 3.39 mmol g<sup>-1</sup> at 75 °C and 1 atm), whereas PEI with  $M_n$  of 10,000 displayed better cyclability, with the adsorbent maintaining its adsorption capacity to an approximately 94 % level over 10 adsorption-desorption cycles. In addition, infusion of PEG into such sorbent system had a positive effect to increasing the capacity by 25.7 %. Chai et al. (Chai et al., 2016) compared the CO<sub>2</sub> adsorption capability of nano-carbon spheres with that of micro-carbon spheres

after PEI incorporation. Analysis conducted at 1 bar and 75 °C revealed a higher CO<sub>2</sub> adsorption capacity for the 45 wt% PEI - loaded carbon nanosphere adsorbent (1.97 mmol g<sup>-1</sup>).

It has been noted from above studies that carbonaceous materials are promising for the development of effective supported PEI CO<sub>2</sub> sorbents. In the case of graphene materials, *in situ* polymerized ethylenimine over hydroxylated graphene support presents enhanced performance (indicative capacity of 4.13 mmol g<sup>-1</sup> (Liu et al., 2015a)). At the same time, graphene/silica hybrid supported PEI sorbent has demonstrated good retaining of capacity (3.89 mmol g<sup>-1</sup>) over cyclic operations (Yang et al., 2013). A great prospect lies in proper pre-modification of various graphene forms, for example, employing advanced techniques such as UV treatment (Varghese et al., 2020). For CNTs, it could be noted that the influence of spacer molecules is advantageous to enhance the performance of supported PEI sorbents, and, indicatively, a capacity of 3.875 mmol g<sup>-1</sup> has been recorded, together with acceptable cyclic stability, heat of adsorption, and kinetics (Deng and Park, 2019). More studies are also needed to investigate the role of surface modification as well as various hybrid combinations of CNTs on the CO<sub>2</sub> capture performance. Among the various carbon materials, the high capture capacity of mesoporous carbon - supported PEI can be noted (4.82 mmol g<sup>-1</sup> indicatively (Wang et al., 2013a)). Furthermore, *in situ* polymerized ethylenimine functionalized mesoporous carbon, combined PEI/K<sub>2</sub>CO<sub>3</sub> impregnated activated carbon, and carbon sphere supported PEI CO<sub>2</sub> sorbents have demonstrated good performance in terms of capture capacity. However, the properties other than capture capacity of carbon material supported PEI sorbents, along with the role of *in situ* synthesis method and modifier/dopant addition, need to be further investigated.

#### 2.4. Alumina – supported PEI

Alumina, or aluminum oxide, has been reported for CO<sub>2</sub> capture due to its ability to contribute *via* both physical and chemical interactions (Chen and Ahn, 2011). The associated distinctive features such as high surface area, widely distributed pore structure and morphologies, acid-base nature, and superior hydrothermal stability are driving forces behind such application for alumina (Chaikittisilp et al., 2011b; Samain et al., 2014). Works on alumina - supported PEI CO<sub>2</sub> sorbents have been reported and are discussed here.

The fabrication of CO<sub>2</sub> solid adsorbents based on PEI - loaded mesoporous  $\gamma$ -alumina possessing high steam stability was reported by Chaikittisilp et al. (Chaikittisilp et al., 2011b). At ambient conditions, the observed adsorption properties were superior for such system as compared to silica based systems. Specifically, for mesoporous  $\gamma$ -alumina with 31 wt% of BPEI, an uptake capacity of ca. 1.41 mmol g<sup>-1</sup> was obtained in 10 % CO<sub>2</sub>, which was reduced by ~16.3 % after the application of 24 h steam exposure at 105 °C, while the observed reduction was ~67.1 % for PEI - loaded mesoporous silica.

Sakwa-Novak et al. (Sakwa-Novak and Jones, 2014) also investigated the CO<sub>2</sub> adsorption performance of mesoporous  $\gamma$ -alumina - supported PEI (BPEI with  $M_w$  of 800). Adsorption analysis performed at 30 °C and 50 % relative humidity revealed an adsorption capacity of ca. 1.71 mmol g<sup>-1</sup> in 400 ppm CO<sub>2</sub>/N<sub>2</sub>. After 12 h of steam exposure, the observed reduction in initial capacity was ~12 %, whereas a 61.5 % reduction was observed after 24 h exposure to steam due to the impact of PEI leaching. A trend towards considerable boehmite generation was also observed during 12 h of steam exposure, which however had no noteworthy impact on the amine efficiency for such solid sorbent.

An alumina monolith supporting PEI was prepared by Sakwa-Novak et al. (Sakwa-Novak et al., 2016) for post-combustion CO<sub>2</sub> capture, while its performance was also compared with that of alumina powder - supported PEI. According to gravimetric data at 30 °C in 400 ppm CO<sub>2</sub>/N<sub>2</sub> mixture, 43–44 wt% BPEI ( $M_w$  = 800) - loaded alumina monolith sorbent demonstrated an adsorption capacity of ca. 0.75 mmol g<sup>-1</sup>, whereas the respective observed capacity for alumina powder was

0.7 mmol g<sup>-1</sup>. After 5 successive adsorption - steam desorption cycles, the observed reduction in CO<sub>2</sub> capacity was lower for the alumina monolith - supported BPEI compared to the alumina powder analogue. A series of steam-stable PEI-filled alumina CO<sub>2</sub> adsorbents was developed by Potter et al. (Potter et al., 2019), and showed that both ordered and disordered mesoporous alumina were appropriate to effectively preserve the capacity drop within the range of 5 %, after loading with 40 wt% of BPEI ( $M_w$  = 800).

#### 2.5. Metal organic framework (MOF) – supported PEI

MOFs are a new class of versatile crystalline materials comprising organic ligand - attached metallic ions or clusters arranged in an open network of extended porosity. CO<sub>2</sub> adsorption performance in terms of capacity, selectivity, and kinetics in MOFs can be tuned on demand by controlling the surface chemical potential as well as pore size and shape through simple organic ligand variations (Adil et al., 2017; Anastasiou et al., 2018; Li et al., 2009; Pokhrel et al., 2018b; Sabouni et al., 2014; Samanta et al., 2011; Sumida et al., 2011). In this section, an overview of literature related to PEI - functionalized MOF CO<sub>2</sub> adsorbent systems is presented.

Enhancement of the dynamic CO<sub>2</sub> capacity and selectivity of UiO-66 after PEI functionalization was observed by Xian et al. (Xian et al., 2015a). For 30 wt% PEI - loaded UiO-66, uptakes of 1.65 and 2.41 mmol g<sup>-1</sup> were acquired in dry and 55 % relative humidity conditions, respectively, at 65 °C, combined with high selectivity values of 111 and 251 in dry and humid conditions, respectively. Upon cyclic adsorption-desorption operation, the capability of the developed adsorbents was maintained to a good extent. An improved CO<sub>2</sub>/N<sub>2</sub> selectivity of 48 and an uptake of 3.2 mmol g<sup>-1</sup> were reported at 298 K and 1 bar by Zhu et al. (Zhu et al., 2019b) for 41 wt% BPEI ( $M_w$  = 600) - functionalized UiO-66-NH<sub>2</sub> developed by Schiff base reaction in the presence of glutaraldehyde. For comparison, UiO-66-NH<sub>2</sub> exhibited a selectivity of 25 and a capacity of 2.7 mmol g<sup>-1</sup>. In addition, the functionalized adsorbent exhibited moisture resistance, cyclic stability, and a moderate heat of adsorption (68 kJ mol<sup>-1</sup> CO<sub>2</sub>).

Darunte et al. (Darunte et al., 2016) carried out functionalization of MIL-101 (Cr) using BPEI with  $M_w$  of 800. Gravimetric CO<sub>2</sub> adsorption studies at 25 °C revealed a capacity of 1.35 mmol g<sup>-1</sup> for BPEI loading of 1.75 mmol g<sup>-1</sup> MOF. Moreover, an amine efficiency of 11 % was acquired for the adsorbent with BPEI content of 0.97 mmol g<sup>-1</sup> MOF. Cyclic studies indicated a rather minor loss of uptake for the adsorbent with 1.06 mmol PEI g<sup>-1</sup> MOF, while the system with PEI loading of 1.1 mmol g<sup>-1</sup> of MOF exhibited also enhanced kinetics. An adsorbent based on 70 wt% PEI ( $M_w$  = 800) - impregnated MIL-101 (Cr) was reported by Mutyala et al. (Mutyala et al., 2019) exhibiting a capacity of 3.81 mmol g<sup>-1</sup> at 75 °C and 1 bar that was raised to 4.4 mmol g<sup>-1</sup> in the presence of moisture due to ammonium bicarbonate generation. The capacity of neat MIL-101 (Cr) was 0.8 mmol g<sup>-1</sup>. This adsorbent system also exhibited appreciable stability under adsorption-desorption cycles, while application of the Avrami model supported the major involvement of chemisorption. At 25 °C and 1 bar, Gaikwad et al. (Gaikwad et al., 2019) recorded a CO<sub>2</sub> uptake of 3 mmol g<sup>-1</sup> for 20 wt % BPEI ( $M_w$  = 800) - impregnated bimetallic MIL-101 (Cr, Mg), whereas the N<sub>2</sub> adsorption was decreased. About 35 % reduction in adsorption performance was observed after exposure in combined humid and acidic (NO<sub>x</sub> and SO<sub>x</sub>) environment. PEI - functionalized MIL-101 was developed by Lin et al. (Lin et al., 2013) exhibiting significant uptake and selectivity even at low pressure. Specifically, selectivity values of 770 and 1200 were obtained at 25 and 50 °C, respectively, for a CO<sub>2</sub>/N<sub>2</sub> mixture at 150 mbar, while the respective capacities were 4.2 and 3.4 mmol g<sup>-1</sup> for 100 wt% LPEI ( $M_w$  = 300) - loaded MIL-101. The observed adsorption kinetics was also enhanced.

Zeolitic imidazolate frameworks (ZIFs) is a subcategory of MOFs consisting of metal cluster - linked imidazole ligands that are topologically analogous to zeolites. Xian et al. (Xian et al., 2015b) highlighted



the positive impact of PEI loading on the CO<sub>2</sub> adsorption of ZIF-8. Indeed, the adsorption capacity of ZIF-8 was increased from 0.126 to 1.61 mmol g<sup>-1</sup> at 65 °C and 1 atm after PEI functionalization (45 wt% of PEI), which was further increased in the influence of moisture. Also, the CO<sub>2</sub>/N<sub>2</sub> selectivity of this adsorbent was increased to 62 from 1.6. This system was thermally stable up to 177 °C. Huang et al. (Huang and Feng, 2018) studied hybrid adsorbents comprising ZIF-8 and PEI-loaded GO for CO<sub>2</sub> capture. Adsorption studies conducted at 273 K and 1 atm revealed a 6-fold enhancement in capacity (181.04 cm<sup>3</sup>/g) as compared to neat GO (26.04 cm<sup>3</sup>/g) and ZIF-8 (30.79 cm<sup>3</sup>/g), which was attributed to the combinatorial effect of PEI functionality and the effective ZIF-8 proliferation in the GO interlayers. A CO<sub>2</sub>/N<sub>2</sub> selectivity value of 184 was reported for this hybrid adsorbent due to the occupancy of amine moieties. Pokhrel et al. (Pokhrel et al., 2018a) studied PEI (*M<sub>w</sub>* = 800) - loaded ZIF-8 obtaining a capture capacity of ca. 0.92 mmol g<sup>-1</sup> at 1 bar and 30 °C in dry CO<sub>2</sub>, while ZIF-8/GO with various modes of functionalizations of the MOF and the GO surfaces were also prepared and studied under dry and humid conditions. Upon impregnation of 40 wt% PEI (*M<sub>w</sub>* = 600) into thermally activated (at 450 °C) Zn/Co ZIF, Cheng et al. (Cheng et al., 2019) achieved a CO<sub>2</sub> capture capacity of 1.82 mmol g<sup>-1</sup> at 298 K and 1 bar, whereas the capacity of unmodified Zn/Co ZIF was only 0.70 mmol g<sup>-1</sup>. Until 9 repeated cycles of adsorption/desorption, the studied adsorbent exhibited an appreciable reversibility as well. The above studies reveal the potential of PEI functionalization to enhance the performance of MOF CO<sub>2</sub> sorbents, specifically, the capture capacity and selectivity of MIL-101, UiO-66-NH<sub>2</sub>, and ZIF-8.

## 2.6. Zeolite – supported PEI

Zeolites, aluminosilicate microporous materials, comprise stable, highly porous network, thus are promising for CO<sub>2</sub> capture applications. To overcome performance limitations originating from moisture influence and increased temperature affects, amine functionalization of zeolites has received particular attention (Cavenati et al., 2004; Khaleel et al., 2018; Samanta et al., 2011; Stuckert and Yang, 2011). Wang et al. (Wang et al., 2018) studied the CO<sub>2</sub> adsorption behavior of rice husk ash sourced ZSM-5 functionalized with PEI. An optimal capacity of 1.96 mmol g<sup>-1</sup> was attained for 30 wt% PEI - modified system at a temperature of 120 °C, with appreciable selectivity and regenerability values. In another work, Lee et al. (Lee et al., 2015a) observed an increase in CO<sub>2</sub> adsorption capacity for ZSM-5 with BPEI loading, with optimum performance obtained for the adsorbents holding 33.3 wt% of BPEI (*M<sub>w</sub>* = 600).

A hybrid adsorbent comprising PEI - functionalized-, mesoporous silica - coated-, zeolite 5A was reported by Liu et al. (Liu et al., 2016). Adsorption experiments performed at 25 °C revealed a high CO<sub>2</sub> uptake of ca. 5.05 mmol g<sup>-1</sup> in 15 % CO<sub>2</sub> for 30 wt% PEI - impregnated adsorbent under the influence of a 70 % relative humidity. Interestingly, the aforesaid adsorption capacity was almost unaffected after 10 successive adsorption-desorption cycles.

## 2.7. Polymer – supported PEI

Porous polymeric materials having large surface area and superior physicochemical characteristics have been explored as support materials for amine based CO<sub>2</sub> adsorbent systems in order to realize effective capture, including in enclosed conditions such as in aircrafts, space shuttles, and submarine, when CO<sub>2</sub> concentration is lower than 1 % (Baugh et al., 2013; Dawson et al., 2011a, b; Samanta et al., 2011; Satyapal et al., 2001; Shi et al., 2017). To this end, PEI has been widely employed for the modification of different porous polymer supports.

PEI - modified porous poly(glycidyl methacrylate) was designed by Han et al. (Han et al., 2015) targeting CO<sub>2</sub> capture from flue gas under highly humid conditions. The resulting adsorbent consisting of 25.4 wt % PEI exhibited an adsorption capacity of ca. 4.85 mmol g<sup>-1</sup> at 40 °C

and 1 bar, combined with appreciable selectivity. Moreover, this system possessed good stability as well as enhanced adsorption kinetics. The influence of moisture had also an enhancing effect on the adsorption performance of the material, which is advantageous for CO<sub>2</sub> capture from flue gas under humidity conditions. In another work, Mane et al. (Mane et al., 2017) reported the preparation of a porous organic polymer adsorbent composed of PEI - modified glycidyl methacrylate. Adsorption studies at 1 bar and 273 K revealed an adsorption capacity of 2.1 mmol g<sup>-1</sup>, along with high CO<sub>2</sub> selectivity. Concerning the regenerability, the capacity of this material was observed to remain almost unaffected up to 4 consecutive adsorption/desorption cycles. Functionalization of poly(methyl methacrylate) mesoporous pellets by PEI infusion was performed by Jung et al. (Jung et al., 2014). Among the various conditions studied, a CO<sub>2</sub> adsorption capacity of 4.26 mmol g<sup>-1</sup> was achieved at 75 °C.

A polymethacrylate resin (HP2MGL) - supported PEI adsorbent was developed by Wang et al. (Wang et al., 2015b). Adsorption studies performed in a fixed-bed column at 0.1 MPa and 25 °C revealed capture capacities of 1.96 and 2.13 mmol g<sup>-1</sup> in 400 and 5000 ppm CO<sub>2</sub>, respectively, for a CO<sub>2</sub> sorbent with 50 wt% of PEI. These values were found to increase under the influence of moisture, whereas the presence of oxygen had a negative effect. Good cyclic stability over 5 consecutive adsorption/desorption cycles was also reported for the aforementioned sorbent system. Nonpolar resin (HP20) was modified by means of PEI impregnation (Chen et al., 2013b). Among various studied compositions, 50 wt% PEI loading yielded enhanced adsorption capacity, faster kinetics, and good recyclability. Specifically, less than 6 min was sufficient to achieve equilibrium at 70 °C, and 4.122 and 2.26 mmol g<sup>-1</sup> loading were obtained at 25 °C and 1 bar for pure CO<sub>2</sub> and a mixture consisting of 400 ppm CO<sub>2</sub>, respectively. Nonlocal density functional theory was also applied to find out the pore size range responsible for CO<sub>2</sub> sorption and it was concluded that the range of 43 – 68 nm granted most of the contribution to the observed sorption capacity.

A capacity of 1.48 mmol g<sup>-1</sup> was reported by Yang et al. (Yang et al., 2019) for 20 % PEI (*M<sub>w</sub>* = 1800) - filled ADS-17 (a commercial nonpolar macroporous polystyrene resin) at 25 °C and 2 bar in 35.6 % CO<sub>2</sub>/CH<sub>4</sub> mixture, together with appreciable regenerability. Meng et al. (Meng et al., 2019) developed a highly CO<sub>2</sub>/CH<sub>4</sub> selective adsorbent for biogas upgrading applications by BPEI (*M<sub>w</sub>* = 1200) loading into NKA-9, a commercial polar macroporous polystyrene resin. A CO<sub>2</sub> uptake of 3.44 mmol g<sup>-1</sup> was observed for the 50 wt% BPEI - loaded adsorbent at 35 °C and 0.45 bar, along with good cyclic and chemical stability.

PEI functionalization of poly(divinylbenzene) possessing hierarchical nanoporous structure was realized by Liu et al. (Liu et al., 2017b). Adsorption studies at 75 °C and ambient pressure revealed an optimal capacity of 3.83 mmol g<sup>-1</sup> for 70 wt% of PEI - loaded nanoporous poly(divinylbenzene). The adsorption capacity was observed to maintain over repeated cyclic operations, while good selectivities were obtained under either dry or humid conditions. In another study, Liu et al. (Liu et al., 2017a) reported PEI functionalization of porous polymer prepared using ethylene glycol dimethacrylate and divinylbenzene. The resulting adsorbent system consisting of 30 wt% of PEI was found to exhibit an uptake of 3.28 mmol g<sup>-1</sup> in dry CO<sub>2</sub> at 25 °C. The capacity was maintained almost unaltered after 8 repeated cycles of adsorption and desorption.

Wang et al. (Wang et al., 2016b) employed macroporous styrene/divinylbenzene - supported PEI as an effective and economic solid sorbent for CO<sub>2</sub> capture. For such sorbent with 70 wt% of PEI loading, CO<sub>2</sub> adsorption capacities of 5.6 and 4.5 mmol g<sup>-1</sup> were observed at 75 °C and 1 bar under pure CO<sub>2</sub> and 10 % mixture, respectively. The capacity was observed to further increase under moisture conditions, while good regenerability was also obtained upon 50 repeated cycles of operation. In another work, Wang et al. (Wang et al., 2017b) reported an adsorbent system based on a polymer nanocomposite comprising PEI - coated TiO<sub>2</sub> nanoparticles and styrene/divinylbenzene porous polymer matrix. A high CO<sub>2</sub> uptake capacity of 5.25 mmol g<sup>-1</sup> was



observed for such solid sorbent with 50 wt% PEI in 10 % CO<sub>2</sub>/10 % H<sub>2</sub>O/N<sub>2</sub> mixture at 75 °C and 1 bar. The developed adsorbent also exhibited only minor capacity reduction upon cyclic operation, appreciable kinetics, and good thermal and mechanical stability. A CO<sub>2</sub> capacity of 4.3 mmol g<sup>-1</sup> was reported by Zhu et al. (Zhu et al., 2019a) for 70 wt% BPEI ( $M_w = 600$ ) - grafted HKUST MOF/poly(divinylbenzene/glycidyl methacrylate) composite adsorbent at 50 °C and 1 atm in pure CO<sub>2</sub>, with a CO<sub>2</sub>/N<sub>2</sub> selectivity of 76 and an appreciable cyclic, thermal and water stability. A relatively low heat of adsorption (48.4 kJ mol<sup>-1</sup>) was recorded for this adsorbent as well.

Aiming at the design of adsorbents possessing enhanced resistance against oxidative degradation, Zhai et al. (Zhai and Chuang, 2017) impregnated crosslinked porous poly(vinyl alcohol) (PVA) with PEI. The authors found that the oxidative resistance ability of this system was superior compared to that of PEI - impregnated SiO<sub>2</sub> upon CO<sub>2</sub> adsorption. This enhancing effect was attributed to hydrogen bonding between the secondary amines of PEI and the -OH groups of PVA, which reduced the degradation tendency of the former. Upon repeated CO<sub>2</sub> adsorption-desorption cycles at 40 and 130 °C, PEI - impregnated porous PVA showed an initial decrease by 25 %, followed by a stabilized trend.

In a recent work, Yin et al. (Yin et al., 2018) developed a CO<sub>2</sub> adsorbent based on PEI - grafted melamine-formaldehyde resin/polyacrylamide blend matrix. For such adsorbent, an uptake of 2.8 mmol g<sup>-1</sup> was realized under dry conditions in 10 % CO<sub>2</sub> at 273 K, which was remained almost unaltered after 18 successive cycles of adsorption/desorption. Zhang et al. (Zhang et al., 2017c) carried out PEI grafting of hydrolyzed porous polyacrylonitrile nanofibers and examined their CO<sub>2</sub> adsorption capability. At 40 °C, the resultant CO<sub>2</sub> adsorbent exhibited a capacity of 1.23 mmol g<sup>-1</sup>, combined with high CO<sub>2</sub>/N<sub>2</sub> selectivity and enhanced regenerability.

Infusion of PEI into 3D aminated carbon nanotube reinforced polyamide was reported by Zainab et al. (Zainab et al., 2017), with the resulting adsorbent system exhibiting a CO<sub>2</sub> adsorption capacity of 1.16 mmol g<sup>-1</sup> at 1 bar and 25 °C for 75 wt% PEI ( $M_w = 10,000$ ) loading. In another work, PEI - loaded hollow fiber polyamideimide sorbents were developed and studied by Li et al. (Li et al., 2013) for post-combustion CO<sub>2</sub> uptake. Of the studied BPEI molecular weights, lower molecular weight ( $M_n = 600$ ) resulted in adsorbents displaying better performance. Specifically, an adsorption capacity of 1.1 mmol g<sup>-1</sup> was realized for a 10 % CO<sub>2</sub>/N<sub>2</sub> mixture under dry conditions at 35 °C and 0.1 bar, which was found to increase to 1.4 mmol g<sup>-1</sup> under humid condition. This material demonstrated good cyclic stability under dry and wet environments as well. PEI - functionalized intrinsic microporous polymers were found to exhibit optimal CO<sub>2</sub> performance when loaded with approximately 20 wt% PEI, yielding adsorption capacities of 1 and 0.2 mmol g<sup>-1</sup> in 14 % and 400 ppm CO<sub>2</sub> mixtures, respectively, at 35 °C (Pang et al., 2015).

A composite foam adsorbent composed of nanofibrillated cellulose and PEI was developed by employing freeze-drying (Sehaqui et al., 2015). At 25 °C, ambient pressure, and 80 % relative humidity, such composite foam holding 44 wt% of BPEI ( $M_r > 600,000$ ) showed a capture capacity of 2.22 mmol g<sup>-1</sup>, which was maintained over cyclic operation. A considerably reduced CO<sub>2</sub> adsorption half-time was also reported for the aforesaid sorbent system. For direct CO<sub>2</sub> adsorption from air, Sujan et al. (Sujan et al., 2019) showed the applicability of a PEI - impregnated cellulose acetate/mesoporous silica composite fiber adsorbent, with breakthrough and pseudo-equilibrium capacities of 0.44 and 0.62 mmol g<sup>-1</sup>, respectively, at 35 °C and 90 scfm in dry conditions, whereas these values were increased to 0.7 and 1.7 mmol g<sup>-1</sup>, respectively, under humid conditions. As seen from the above literature analysis, a series of porous polymer supported PEI sorbents has been investigated for CO<sub>2</sub> capture. Distinctively, polymethacrylates (glycidyl and methyl versions), polydivinylbenzene, and polystyrene (polar version) - based porous materials have presented promising performance among the available materials.

## 2.8. Additional materials with PEI

Additional PEI based adsorbents using materials that are not included in the aforementioned categories are discussed in this section. PEI - functionalized titanate nanotubes (TNTs) were developed by Guo et al. (Guo et al., 2016) by first preparing protonated TNTs, followed by wet impregnation with BPEI ( $M_w = 600$ ). The resulting nanostructured adsorbent consisting of 50 wt% BPEI exhibited a good CO<sub>2</sub> uptake capacity of 3.06 mmol g<sup>-1</sup> at 75 °C using a 10 % CO<sub>2</sub> mixture. A 20 wt% PEI - loaded MgCO<sub>3</sub> adsorbent with an uptake of 1.07 mmol g<sup>-1</sup> at 75 °C was reported by Wan et al. (Wan et al., 2019), along with appreciable regenerability. The adsorption performance was enhanced by 19 % in the presence of 10 % water vapor.

Li et al. (Li et al., 2017) examined the potential of PEI - functionalized magnetic nanoparticles for CO<sub>2</sub> capture applications. The results obtained underlined the effectiveness of PEI loading to enhancing capture capacity, selectivity, and regenerability of the magnetic nanoparticles. Compared to LPEI, BPEI was found to yield higher adsorption capacity. Specifically, the adsorbent with 16 % BPEI ( $M_w = 25,000$ ) exhibited a CO<sub>2</sub> uptake of 0.36 mmol g<sup>-1</sup> at 25 °C. The relatively low capacity is attributed to lack of extended porosity in the magnetic particle cores. In another work, Liu et al. (Liu et al., 2013c) studied the CO<sub>2</sub> capture performance of silane - modified-, PEI - functionalized-, Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles. The resulting adsorbent exhibited a capacity of 0.373 mol L<sup>-1</sup> at 40 °C and 100 kPa, combined to fast sorption kinetics, adequate selectivity, and appreciable cyclic stability.

## 3. Polypropylenimine-based adsorbents

Polypropylenimine (PPI), also known as polyazetidine, is an appealing class of polymeric amines available in linear, branched, or dendritic forms (De Brabander et al., 1996; Knowles and Chaffee, 2016). PPI accommodates primary, secondary, and tertiary amines at corresponding chain ends, backbone, and branch points, which support its potential for CO<sub>2</sub> capture (Table 1) (Pang et al., 2017; Sarazen and Jones, 2017). However, only limited attempts have been reported on PPI - based CO<sub>2</sub> sorbent systems because of the complications associated to monomer synthesis and polymerization time (Sarazen and Jones, 2017; Schacht and Goethals, 1974). This section reviews available works reported for supported PPI - based CO<sub>2</sub> adsorbents.

A branched PPI composite of SBA-15 was developed by Sarazen et al. (Sarazen and Jones, 2017) for CO<sub>2</sub> adsorption. According to the experimental data, an adsorption capacity of 0.93 mmol g<sup>-1</sup> was observed for a composite sorbent with 0.39 wt% of organic content at 308 K when exposed to 10 % CO<sub>2</sub> mixture. This adsorption capacity value was lower as compared to analogous PEI - impregnated SBA-15 (1.5 mmol g<sup>-1</sup>). The authors also investigated the effect of increase in polymerization time and temperature on the CO<sub>2</sub> adsorption and found a decreasing tendency of the PPI - modified SBA-15 due to the continuous conversion of primary amines to tertiary amines. In addition, basic resin treatment of PPI was advantageous to enhance the CO<sub>2</sub> capture potential in comparison to ammonium hydroxide treatment. Pang et al. (Pang et al., 2017) compared the performance of solid CO<sub>2</sub> adsorbents prepared using SBA-15 - supported linear- as well as dendritic PPI with those of SBA-15/PEI sorbents. In that work, the CO<sub>2</sub> adsorbents with PPI displayed not only higher capacity and amine efficiency but also enhanced oxidation resistance. The role of various acid initiators on the performance of PPI/SBA-15 composite adsorbents was examined by Sarazen et al. (Sarazen et al., 2019). Accordingly, a capacity of 0.31, 0.25, 0.15 and 0.17 mmol g<sup>-1</sup> was obtained at 303 K in 400 ppm CO<sub>2</sub> feed for 30 wt% branched PPI - containing adsorbent prepared using HClO<sub>4</sub>, HBr, HCl and CH<sub>3</sub>SO<sub>3</sub>H, respectively. The amine efficiency was 0.039, 0.04, 0.025 and 0.026 mmol CO<sub>2</sub>/mmol N<sub>2</sub>, respectively. The oxidation stability of the developed adsorbents was studied by exposure in air at 383 K for 12 h, and a reduction of 24 % in the initial capacity was recorded for the HBr - based adsorbent, though

Table 4

Summarized adsorption properties for CO<sub>2</sub> sorbents based on polypropylenimine, polyallylamine, polyaniline, amino dendrimers, and hyperbranched polyamines (PPI: polypropylenimine; PAA: polyallylamine; APTES: (3-aminopropyl)triethoxysilane; GO: graphene oxide; MWCNs: multi-walled carbon nanotubes; GC: gas chromatography; MS: mass spectrometer; MSB: magnetic suspension balance).

Polymeric amine	Support	Adsorption capacity (mmol g <sup>-1</sup> )	Conditions	Method	Remarks	Reference
30 wt% branched PPI	SBA-15	0.93	34.85 °C, 10 % CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	<ul style="list-style-type: none"> <li>Lower capacity than that of PEI - loaded SBA-15.</li> <li>Decrease in capacity with increase in polymerization time and temperature.</li> <li>Amine efficiency of 0.039 mmol CO<sub>2</sub>/mmol N.</li> <li>Capacity of 1.14 mmol g<sup>-1</sup> in 10% CO<sub>2</sub>/N<sub>2</sub> mixture.</li> <li>Better capacity compared to other initiators, namely HBr, HCl and CH<sub>3</sub>SO<sub>3</sub>H.</li> <li>Higher capacity in moisture influence, whereas only 0.82 mmol g<sup>-1</sup> in dry condition.</li> <li>Better performance compared to PPI dendrimers with M<sub>w</sub> of 300 and 1622.</li> <li>Higher amine efficiency for 50 wt% PAA.</li> <li>Benefits in terms of thermal and oxidative stabilities compared to PEI - based system.</li> </ul>	(Sarazen and Jones, 2017)
30 wt% branched PPI with HClO <sub>4</sub> as acid initiator	SBA-15	0.31	34.85 °C, 400 ppm CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	<ul style="list-style-type: none"> <li>Amine efficiency of 0.039 mmol CO<sub>2</sub>/mmol N.</li> <li>Capacity of 1.14 mmol g<sup>-1</sup> in 10% CO<sub>2</sub>/N<sub>2</sub> mixture.</li> <li>Better capacity compared to other initiators, namely HBr, HCl and CH<sub>3</sub>SO<sub>3</sub>H.</li> <li>Higher capacity in moisture influence, whereas only 0.82 mmol g<sup>-1</sup> in dry condition.</li> <li>Better performance compared to PPI dendrimers with M<sub>w</sub> of 300 and 1622.</li> <li>Higher amine efficiency for 50 wt% PAA.</li> <li>Benefits in terms of thermal and oxidative stabilities compared to PEI - based system.</li> </ul>	(Sarazen et al., 2019)
PPI dendrimer (M <sub>w</sub> = 741) (PPI to GO weight ratio of 3)	GO	2	36.85 °C, 1 atm, water vapor relative pressure of 0.35	Gravimetric set-up	<ul style="list-style-type: none"> <li>Higher capacity in moisture influence, whereas only 0.82 mmol g<sup>-1</sup> in dry condition.</li> <li>Better performance compared to PPI dendrimers with M<sub>w</sub> of 300 and 1622.</li> <li>Higher amine efficiency for 50 wt% PAA.</li> <li>Benefits in terms of thermal and oxidative stabilities compared to PEI - based system.</li> </ul>	(Tsoufis et al., 2014)
65 wt% PAA (M <sub>n</sub> = 15000)	SBA-15	2.47	140 °C, 1 atm, 99.99 % CO <sub>2</sub>	Gravimetric	<ul style="list-style-type: none"> <li>Higher amine efficiency for 50 wt% PAA.</li> <li>Benefits in terms of thermal and oxidative stabilities compared to PEI - based system.</li> </ul>	(Wang et al., 2017a)
70 wt% PAA	Fumed silica	4.28	21 °C, 1.21 atm, 10 % CO <sub>2</sub> /N <sub>2</sub> mixture	Adsorption-desorption equipment	Poor adsorption kinetics than those of systems with lower PAA loading.	(Zerze et al., 2017)
41 wt% PAA	Silica foam	1.56	25 °C, 10 % CO <sub>2</sub> /Ar mixture	Gravimetric	<ul style="list-style-type: none"> <li>Decrease in capacity with further increase in PAA loading.</li> <li>Appreciable CO<sub>2</sub> selectivity.</li> <li>Capacity of 0.86 mmol g<sup>-1</sup> in 400 ppm CO<sub>2</sub>.</li> <li>Comparable capacity until 75 °C compared to guanidylated PAA - functionalized system, and beyond that a better performance for guanidylated PAA.</li> <li>Better regenerability for guanidylated PAA.</li> <li>Lower capacity compared to PEI (M<sub>w</sub> = 800) - loaded system.</li> <li>Higher oxidation stability for PAA - loaded system.</li> <li>Drop in capacity of only less than 10 % after various oxidation treatments.</li> </ul>	(Chaikititilip et al., 2011a)
32 wt% PAA	Silica foam	1.53	25 °C, 10 % CO <sub>2</sub> /He mixture	Gravimetric	<ul style="list-style-type: none"> <li>Capacity of 0.86 mmol g<sup>-1</sup> in 400 ppm CO<sub>2</sub>.</li> <li>Comparable capacity until 75 °C compared to guanidylated PAA - functionalized system, and beyond that a better performance for guanidylated PAA.</li> <li>Better regenerability for guanidylated PAA.</li> <li>Lower capacity compared to PEI (M<sub>w</sub> = 800) - loaded system.</li> <li>Higher oxidation stability for PAA - loaded system.</li> <li>Drop in capacity of only less than 10 % after various oxidation treatments.</li> </ul>	(Alkhabbaz et al., 2014)
45.8 wt% PAA	γ-alumina	1.07	50 °C, 10 % CO <sub>2</sub> /He mixture	Gravimetric	<ul style="list-style-type: none"> <li>Better regenerability for guanidylated PAA.</li> <li>Lower capacity compared to PEI (M<sub>w</sub> = 800) - loaded system.</li> <li>Higher oxidation stability for PAA - loaded system.</li> <li>Drop in capacity of only less than 10 % after various oxidation treatments.</li> </ul>	(Bali et al., 2013)
60 wt% PAA	Polyacrylonitrile fibers	6.22	22 °C, 15.2 % CO <sub>2</sub> /N <sub>2</sub> mixture	Three-line adsorption system connected to GC	Other benefits such as faster adsorption kinetics, reduced regeneration temperature, and thermal stability.	(Yang et al., 2010b)
Polyaniline (APTES - functionalized silicone based one)	-	3	34.85 °C, 1.10 atm, 15.03 % CO <sub>2</sub> /N <sub>2</sub> mixture	Micro-Balance Thermo D-200	<ul style="list-style-type: none"> <li>Respective CO<sub>2</sub> purity and recovery of 47.65 % and 92.46 %.</li> </ul>	(Yang et al., 2014)
Polyaniline	Graphite-sourced GO	3.2	26.85 °C, 20 bar, 99.99 % CO <sub>2</sub>	High-pressure sorption analyzer (ISOSORP GAS LP-flow, Rubotherm) connected with a MSB	<ul style="list-style-type: none"> <li>Offered benefits in terms of reversibility, fast kinetics, and thermal stability.</li> <li>A capacity of 2.5 mmol g<sup>-1</sup> for analogous carbon nanofiber-sourced GO.</li> <li>Increase in microporosity of GO after polyaniline introduction.</li> <li>CO<sub>2</sub>/N<sub>2</sub> selectivity of 20-21.</li> <li>Drop in capacity with increase in temperature.</li> <li>Good cyclic stability.</li> <li>Good regenerability at 140 °C.</li> </ul>	(RODRÍGUEZ-GARCÍA et al., 2019)
Nanostructured polyaniline	HNO <sub>3</sub> - treated graphene	75	25 °C, 11 bar	Sievert's apparatus	<ul style="list-style-type: none"> <li>Drop in capacity with increase in temperature.</li> <li>Good cyclic stability.</li> <li>Good regenerability at 140 °C.</li> </ul>	(Mishra and Ramaprabhu, 2012a)
Polyaniline	HNO <sub>3</sub> - treated MWCNs	67	25 °C, 11 bar	Sievert's apparatus	<ul style="list-style-type: none"> <li>Drop in capacity with increase in temperature.</li> <li>Good cyclic stability.</li> <li>Good regenerability at 140 °C.</li> </ul>	(Mishra and Ramaprabhu, 2012b)

(continued on next page)

Table 4 (continued)

Polymeric amine	Support	Adsorption capacity (mmol g <sup>-1</sup> )	Conditions	Method	Remarks	Reference
Polyaniline (aniline to magnetite nanocapsules weight ratio of 1)	Magnetite nanocapsules	54.21	28 °C, 14.5 bar	Sievert's apparatus	<ul style="list-style-type: none"> <li>● Faster adsorption kinetics.</li> <li>● Heat of adsorption of ca. 7 kJ mol<sup>-1</sup>.</li> <li>● Maintained capacity and kinetics over 15 cycles.</li> </ul>	(Tamilarasan and Ramaprabhu, 2012)
Polyaniline	MIL-101(GT)	3.9	24.85 °C, 1 atm, 99.99 % CO <sub>2</sub>	Gas/vapor adsorption measurement instrument (BELSORP-max, Bel-Japan)	<ul style="list-style-type: none"> <li>● CO<sub>2</sub>/N<sub>2</sub> selectivity of 14.</li> <li>● Capacity of 1.7 mmol g<sup>-1</sup> at 0.15 atm.</li> </ul>	(Yoo et al., 2018)
Poly(amido amine) dendrimer (generation 4 and M <sub>w</sub> = 14213) (poly(amido amine) dendrimer to laponite weight ratio of 0.7)	Laponite	0.48	30 °C, 60 % CO <sub>2</sub> /N <sub>2</sub> mixture	Gravimetric	<ul style="list-style-type: none"> <li>● CO<sub>2</sub> adsorption enthalpy of ca. 51 kJ mol<sup>-1</sup>.</li> <li>● Better performance than those of sericite and hydrotaclite - based systems.</li> </ul>	(Shah et al., 2015)
Tris(2-aminoethyl)amine dendrimer (generation 3)	SBA-15	1.82	25 °C, 1 atm, 99.99 % CO <sub>2</sub>	Gravimetric	<ul style="list-style-type: none"> <li>● Favorable regenerability and thermal stability.</li> </ul>	(Bhagyalakshmi et al., 2010)
Melamine amino-dendrimer (generation 3 and 44.4 wt%)	SBA-15	0.98	20 °C, 90 % CO <sub>2</sub> /Ar mixture	Gravimetric	<ul style="list-style-type: none"> <li>● Highly appreciable CO<sub>2</sub> selectivity.</li> <li>● Complete desorption at 105 °C.</li> </ul>	(Liang et al., 2008)
Melamine amino-dendrimer (generation 4 and 55 wt %)	Silica foam	0.87	25 °C, 90 % CO <sub>2</sub> /Ar mixture	Gravimetric	Enhanced heat of adsorption and thermal stability.	(Liang et al., 2009)
Acrylate ethylenediamine dendrimer (generation 3)	Propylamine - functionalized SBA-15	0.45	30 °C, 12 % CO <sub>2</sub> /N <sub>2</sub> mixture	Fixed bed flow instrument	–	(Jing et al., 2014)
Melamine diethylenetriamine dendrimer (generation 2)	Propylamine - functionalized SBA-15	0.54	30 °C, 12 % CO <sub>2</sub> /N <sub>2</sub> mixture	Fixed bed flow instrument	Better capacity than those of systems based on melamine ethylenediamine and melamine triethylenetriamine dendrimers.	(Jing et al., 2014)
CO <sub>2</sub> - imprinted hyperbranched polyamine based on tetraethylenepentamine	–	7.65	25 °C, 10 % CO <sub>2</sub> /N <sub>2</sub> mixture	Adsorption column connected with GC	Better performance than those of hyperbranched polyamines and CO <sub>2</sub> - imprinted versions based on triethylenetriamine and diethylenetriamine.	(He et al., 2016)
Hyperbranched polyamine based on aziridine (prepared via ring opening polymerization)	SBA-15	5.6	25 °C, humidified 10 % CO <sub>2</sub> /Ar mixture	Packed bed flow reactor connected with MS	Higher capacity at 25 °C than that at 75 °C.	(Drese et al., 2009)
Hyperbranched polyamine based on aziridine (prepared via vapor-phase transport means)	SBA-15	0.93	25 °C, 10 % CO <sub>2</sub> /He mixture	Gravimetric	Maintained capacity over cyclic operations.	(Chaikittisilp et al., 2013)
Hyperbranched polyamine based on pentaethylenhexamine and acrylamide	Polypropylene fibers with acrylamide functionalities	5.64	25 °C, 10 % CO <sub>2</sub> /N <sub>2</sub> mixture	Adsorption column connected with GC	<ul style="list-style-type: none"> <li>● Amine efficiency of 88.2 %.</li> <li>● Other benefits such as reduced CO<sub>2</sub> transfer resistance and robust regenerability.</li> </ul>	(He et al., 2017)

a 64 % reduction was marked for the  $\text{HClO}_4$  - based one.

Intercalation of PPI dendrimer into GO layers was performed by Tsoufis et al. (Tsoufis et al., 2014). Under wet conditions, this adsorbent showed enhanced adsorption capacity as well as kinetics. Accordingly, at 37 °C and atmospheric pressure, an adsorption capacity of 2 mmol  $\text{g}^{-1}$  was observed for the intercalated adsorbent composed of GO to PPI dendrimer weight ratio of 1:3. The reported adsorption properties of PPI - based  $\text{CO}_2$  sorbents are summarized in Table 4.

It has been revealed from the above discussion that only a few reports are available on PPI - based  $\text{CO}_2$  sorbent materials mainly due to the challenges associated to monomer as well as polymer synthesis. Therefore, emphasis has to be dedicated to effectively sort out these challenges first and then proceed to expand to a wide spectrum of various supported PPI  $\text{CO}_2$  sorbent systems.

#### 4. Polyallylamine-based adsorbents

Polyallylamine (PAA) is an attractive category of polymeric amines with its molecular structure consisting of highly dense primary amines at the side chain (Table 1) (Cai et al., 2008; Carretti et al., 2003). For  $\text{CO}_2$  capture applications, PAA - functionalized systems have been introduced to alleviate the issues associated to oxidative and thermal resistance. Additionally, PAA finds suitability as a good binding material in the supported amine systems because of cohesive forces among the chains as well as adhesive forces with supports (Alkhabbaz et al., 2014; Chaikittisilp et al., 2011a; Klinthong et al., 2014). In this section, we overview available studies related to PPA - based  $\text{CO}_2$  sorbent systems.

Wang et al. (Wang et al., 2017a) reported PAA impregnation into mesoporous SBA-15. Because of its unique macromolecular structure, PAA offered more benefits related to rigidity and steric resistance compared to PEI after introduction into SBA-15 pores. According to gravimetric adsorption studies, the  $\text{CO}_2$  adsorption capacity of PAA - impregnated SBA-15 was observed to increase with temperature. Indicatively, a capacity of 2.47 mmol  $\text{g}^{-1}$  was achieved for 65 wt% PAA - impregnated sorbent at a temperature of 140 °C and a pressure of 1 atm. Regarding PAA content, for up to 65 wt% loading, the adsorption capacity of the resultant adsorbent was increased, followed by a decreasing trend. However, the 50 wt% PAA - loaded system exhibited superior amine efficiency. The authors also investigated the role of humidity and noted a positive effect in terms of adsorption capacity and cyclability. Moreover, as compared to PEI - modified systems, the observed thermal and oxidative degradation resistance was higher for PAA. These observations are described in Fig. 6. Considering the sorption kinetics, the performance of PAA - modified sorbent system was relatively weak.

A PAA-NaOH mixture was used as a binder solution for the generation of pellets of APTES - grafted on mesoporous MCM-41 (Klinthong et al., 2014). The introduction of 3 % PAA and 2 % NaOH upon pelletizing was found to improve the mechanical strength and thermal stability of APTES - grafted MCM-41. Indeed, the observed mechanical strength was above 0.45 MPa with a high durability. In addition, the capture capacity was observed to be maintained with a recovery rate of more than 90 %.

PAA functionalization of fumed silica was developed for  $\text{CO}_2$  capture at ambient conditions (Zerze et al., 2017). At 21 °C and 123 kPa, such nanocomposite with 70 wt% PAA showed a  $\text{CO}_2$  capture capacity of 4.28 mmol  $\text{g}^{-1}$  under a humid 10 %  $\text{CO}_2/\text{N}_2$  mixture, yet exhibiting lower adsorption kinetics than analogous adsorbents with lower PAA loading. The 30 and 50 wt% PAA - loaded sorbents were particularly suitable for  $\text{CO}_2$  capture at ambient conditions with the 30 wt% PAA system exhibiting enhanced regenerability as well (more than 92 %).

In another work, PAA was synthesized and impregnated into mesoporous silica foam (Chaikittisilp et al., 2011a). At 25 °C, an adsorption capacity of 1.56 mmol  $\text{g}^{-1}$  was observed for a 41 wt% PAA - loaded sample using a 10 %  $\text{CO}_2$  mixture, while a decreasing trend in

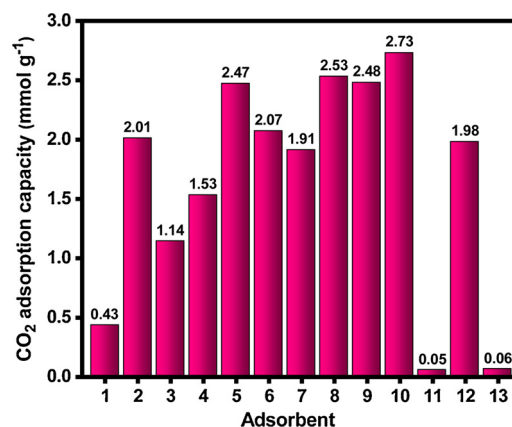


Fig. 6. Gravimetrically determined adsorption capacity for the below types of polyallylamine (PAA)-modified adsorbents: (1) 50 % PAA - SBA-15 at 75 °C, (2) 50 % PAA - SBA-15 at 140 °C, (3) heat treated 50 % PAA - SBA-15 at 140 °C, (4) 40 % PAA - SBA-15 at 140 °C, (5) 65 % PAA - SBA-15 at 140 °C, (10) 50 % LPEI - SBA-15 at 75 °C, (11) heat treated 50 % LPEI - SBA-15 at 75 °C, (12) 50 % BPEI - SBA-15 at 75 °C, and (13) heat treated 50 % BPEI - SBA-15 at 75 °C. Fixed-bed sorption system generated adsorption capacity for (6) 50 % PAA - SBA-15 at 75 °C in dry  $\text{CO}_2$ , (7) 50 % PAA - SBA-15 at 75 °C in dry  $\text{CO}_2$  after 10 cycles, (8) 50 % PAA - SBA-15 at 75 °C in humid  $\text{CO}_2$ , and (9) 50 % PAA - SBA-15 at 75 °C in humid  $\text{CO}_2$  after 10 cycles.

adsorption capacity was noted beyond this PAA loading. The authors also supported that this adsorbent would be of high potential to capture  $\text{CO}_2$  selectively from air. A comparative study on the functionalization of mesoporous silica foam using PAA and its guanidinylation version was reported by Alkhabbaz et al. (Alkhabbaz et al., 2014). The adsorption capacity for both samples was found to decrease with temperature. Up to 75 °C, a comparative adsorption capacity was noted for both, whereas beyond 75 °C, a better performance was yielded for the guanidinylation PAA - functionalized system. Indicatively, an adsorption capacity of 1.4 mmol  $\text{g}^{-1}$  at 25 °C was observed for systems with 35 % organic loading using a 10 %  $\text{CO}_2$  mixture, though at 140 °C, 0.6 and 0.9 mmol  $\text{g}^{-1}$  were observed for PAA and guanidinylation PAA - modified systems, respectively. With respect to regenerability, guanidinylation PAA - modified silica foam presented superior performance when regenerated at 120 °C. Fig. 7 compares the reported features of PAA- and guanidinylation PAA - modified silica foam  $\text{CO}_2$  sorbents.

Bali et al. (Bali et al., 2013) examined the oxidation stability of mesoporous  $\gamma$ -alumina - supported PAA adsorbents and compared the performance with PEI - loaded analogous systems. According to the results obtained after various oxidation treatments, higher oxidation

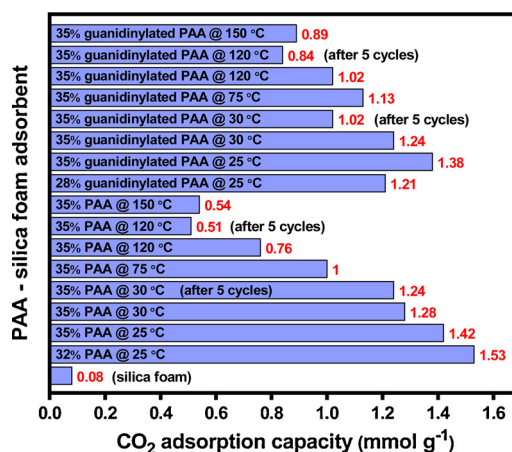


Fig. 7.  $\text{CO}_2$  adsorption capacity for polyallylamine (PAA) - and guanidinylation PAA - modified silica foam in various conditions.



stability was observed for a PAA - based sorbent than that of the PEI - based one. The decrease in CO<sub>2</sub> capture capacity for the former system was less than 10 % as compared to its initial capacity of 1.07 mmol g<sup>-1</sup> obtained at 50 °C, due to the influence of more number of primary amines. Fabrication of PAA - grafted polyacrylonitrile fiber adsorbents exhibiting enhanced uptake capacity, regenerability, thermal stability, faster adsorption kinetics and reduced temperature of regeneration were reported by Yang et al. (Yang et al., 2010b). Indicatively, a high CO<sub>2</sub> uptake capacity of ca. 6.22 mmol g<sup>-1</sup> at 22 °C was obtained for such an adsorbents with 60 wt% of PAA grafting. Table 4 summarizes the adsorption properties of the various PAA - based CO<sub>2</sub> sorbent systems.

Above reports reveal the promising influence of PAA to exhibit improved CO<sub>2</sub> sorption properties, for example, a capture capacity of 6.22 mmol g<sup>-1</sup> at 22.5 °C (Yang et al., 2010b) and 4.28 mmol g<sup>-1</sup> at 21 °C and 1.23 bar (Zerze et al., 2017) is recorded for respective polyacrylonitrile fibers and fumed silica - supported PAA sorbents. Furthermore, PAA - based sorbent systems exhibited better stability in oxidative and thermal conditions in comparison to supported PEI CO<sub>2</sub> sorbents. In certain cases, PAA functionalization may pose limitations due to slow kinetics, which, if not overcome, can impact the throughput and design of the capture process with respect to cyclic operation both upon adsorption as well as during the desorption step. Indeed, an important parameter towards development of scalable adsorbents is to exhibit fast kinetics, which often is compromised in PAA-based systems despite their high capacity, due to diffusion limitations of CO<sub>2</sub> through the densely packed polymeric chains on the surface. In this regard, controlled grafting needs to be realized so that transport pathways are not blocked, while further studies are recommended focusing on addition of CO<sub>2</sub>-philic modifiers and dopants, in such supported adsorbent systems.

## 5. Polyaniline-based adsorbents

Polyaniline is a conducting polymer with repeating unit consisting of secondary amine in between two aromatic benzene rings (Table 1). Ease of synthesis, ability to tune its morphology into different nanostructures with large surface area, and superior thermal stability render it promising for various applications (Ansari and Keivani, 2006; Blinova and Svec, 2012; Huang et al., 2003; Liu et al., 2012b; Zhao et al., 2012b). Works on polyaniline - based CO<sub>2</sub> adsorbents are discussed in this section.

A polyaniline (APTES - functionalized silicone based one) CO<sub>2</sub> adsorbent (Yang et al., 2014) exhibited a CO<sub>2</sub> capacity of 3 mmol g<sup>-1</sup> at 35 °C and 1.1 atm when exposed to a 15 % CO<sub>2</sub>/N<sub>2</sub> mixture. In addition to supporting the experimental evidence with simulation data, the authors studied also the regeneration behavior of the developed adsorbents. Indeed, Temperature Swing Adsorption (TSA) studies revealed a recovery of 92.46 % and a CO<sub>2</sub> purity of 47.65 % in a single-bed after five steps using 35 °C and 110 °C for the adsorption and desorption steps, respectively, and 1.1 atm as feed pressure. In another work, Chou et al. (Chou et al., 2014) found a superior performance of the aforementioned adsorbent when Pressure Swing Adsorption (PSA) was used compared to TSA at low CO<sub>2</sub> feed concentration. Indeed, a CO<sub>2</sub> purity of 97.13 % and a recovery of 87.26 % were obtained in single-bed, three-step PSA under operating pressures of 6, 1, and 0.1 atm for the feed, co-current depressurization, and vacuum pressures, respectively. A hybrid hypercrosslinked porous polyaniline by means of Friedel-Crafts reaction using octavinylsilsesquioxane, with a CO<sub>2</sub> capture capacity of 0.59 mmol g<sup>-1</sup> at 298 K and 1 bar, and a BET surface area of 461 m<sup>2</sup> g<sup>-1</sup> was reported by Tang et al. (Tang et al., 2019)

A polyaniline-GO nanocomposite adsorbent using graphite-sourced GO was developed by Rodriguez-Garcia et al. (RODRÍGUEZ-GARCÍA et al., 2019) with a capacity of 3.2 mmol g<sup>-1</sup> at 300 K and 20 bar exhibiting good reversibility, kinetics, and thermal stability. For

comparing, a capacity of 2.5 mmol g<sup>-1</sup> was obtained for an analogous polyaniline nanocomposite adsorbent based on carbon nanofiber-sourced GO. The observed CO<sub>2</sub>/N<sub>2</sub> selectivity for these adsorbents was in the range of 20–21. Interestingly, an increase in microporosity was noticed upon polyaniline introduction onto GO contributing to the enhancement of the CO<sub>2</sub> adsorption capacity.

Nanostructured polyaniline - modified graphene, which was prepared by chemical means in HCl with the aid of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, was studied for reversible CO<sub>2</sub> capture (Mishra and Ramaprabhu, 2012a). To assist in functionalization, graphene sheets were treated in HNO<sub>3</sub> after hydrogen-mediated thermal exfoliation of GO. A high CO<sub>2</sub> adsorption capacity of 75 mmol g<sup>-1</sup> was obtained at 25 °C and 11 bar owing to the influence of CO<sub>2</sub>-philic groups of polyaniline. Though, a decreasing trend in capacity was observed with increasing temperature, capacities of 47 and 31 mmol g<sup>-1</sup> were still obtained at 50 and 100 °C at the same pressure conditions, respectively, coupled to superior cyclability. MWCNTs were also decorated with polyaniline targeting reversible CO<sub>2</sub> capture applications (Mishra and Ramaprabhu, 2012b). In order to obtain an effective anchoring of polyaniline on the surface of the CNTs, additional oxygen containing functionalities were introduced by treatment in concentrated HNO<sub>3</sub>. Due to the optimized occupancy of polyaniline molecules on the MWCNTs surface, the resultant nanocomposite exhibited high adsorption capacity values of 67, 46, and 27 mmol g<sup>-1</sup> at 25, 50, and 100 °C, respectively and at elevated pressures (11 bar). This nanocomposite adsorbent also showed high regenerability potential at temperature of ca. 140 °C.

Polyaniline-magnetite nanocapsules were fabricated by Tamilarasan et al. (Tamilarasan and Ramaprabhu, 2012) targeting mainly capture at high pressure conditions. Due to contribution of both physical and chemical adsorption, the resulting nanocomposite (50 wt% aniline) showed a capacity of 54.21 mmol g<sup>-1</sup> at 28 °C and 14.5 bar, exhibiting also fast adsorption kinetics. Notably, a low heat of adsorption was also observed, which supports physisorption as the main contributor to the adsorption. Furthermore, this nanocomposite sorbent was found to possess good thermal stability and cyclability as it could maintain its adsorption capacity and kinetics after 15 adsorption-desorption cycles. The reported performance of polyaniline - based CO<sub>2</sub> adsorbents is listed in Table 4 and depicted in Fig. 8.

A polyaniline/MIL-101(Cr) composite adsorbent was reported by Yoo et al. (Yoo et al., 2018) exhibiting an uptake of 3.9 mmol g<sup>-1</sup> and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 14 at 1 atm and 298 K, for an adsorbent prepared using 5 mM aniline hydrochloride solution. At low pressure (0.15 atm), a capacity of 1.7 mmol g<sup>-1</sup> was obtained. The regenerability of the prepared CO<sub>2</sub> adsorbent was examined after 5 repeated adsorption-desorption cycles, while an enthalpy of adsorption of 51 kJ mol<sup>-1</sup> was observed. A polyaniline/SBA-15 nanocomposite adsorbent was prepared by Boukoussa et al. (Boukoussa et al., 2018), who observed an increase in CO<sub>2</sub> affinity with amount until 30 wt% of polyaniline loading owing to the enhanced action of chemisorption.

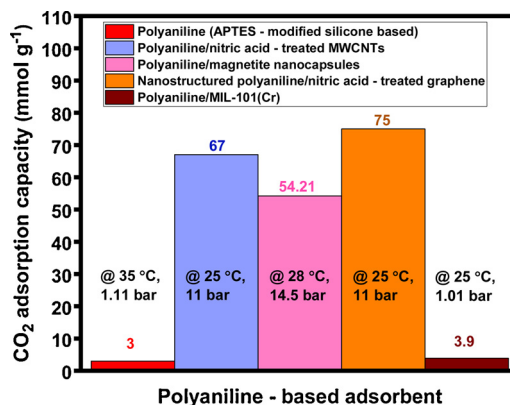


Fig. 8. CO<sub>2</sub> adsorption capacity for polyaniline - based adsorbents.

The above investigations support the applicability of polyaniline - based sorbents for CO<sub>2</sub> capture, with high potential particularly at higher pressures. For instance, a capture capacity as high as 75 mmol g<sup>-1</sup> (Mishra and Ramaprabhu, 2012a) is recorded for nanostructured polyaniline - modified graphene. More CO<sub>2</sub> sorbents based on polyaniline are suggested to be developed in order to further explore the observed potential and overcome current challenges.

## 6. Amino-dendrimer – based adsorbents

Dendrimers, also termed as arborols or cascade molecules, are 3-dimensional macromolecular structures consisting of highly branched repeating units in a regular order around a central core (Bosman et al., 1999; Fischer and Vögtle, 1999). Their size, chemical functionality, and molecular weight can be tuned on demand upon synthesis (Fischer and Vögtle, 1999; Lu et al., 2006; Newkome et al., 2001; Reynhardt et al., 2004). Amino-dendrimers are an attractive subcategory of this family exhibiting high amine or nitrogen density (Jing et al., 2014; Lu et al., 2006) (Table 1). This section covers available studies related to CO<sub>2</sub> capture using various amino dendrimers - based adsorbents.

Incorporation of poly(amido amine) dendrimer into clays was reported by Shah et al. (Shah et al., 2015) using three different clays, namely laponite, hydrotaclite and sericite. The modified laponite showed higher adsorption capacity compared to the other studied clays. For a dendrimer to laponite weight ratio of 0.7, the observed adsorption capacity was 0.478 mmol g<sup>-1</sup> at 30 °C. Grafting of SBA-15 by a tris(2-aminoethyl)amine dendrimer (Bhagiyalakshmi et al., 2010) yielded CO<sub>2</sub> capture capacities of 1.82 and 1.37 mmol g<sup>-1</sup> at 25 °C and 1 atm for the so called third and second generation dendrimer - grafted SBA-15, respectively, while the resulting functionalized adsorbents also exhibited enhanced regenerability and thermal stability. The contribution from primary amines in melamine amino-dendrimers - loaded on SBA-15 was also explored (Liang et al., 2008). Indicatively, a CO<sub>2</sub> adsorption capacity of 0.98 mmol g<sup>-1</sup> was reported at 20 °C for SBA-15 modified with third generation melamine dendrimers, exhibiting also good selectivity and a heat of adsorption in the range of 51 – 70 kJ mol<sup>-1</sup>, with an almost complete desorption being realized at 105 °C. In another study, Liang et al. (Liang et al., 2009) developed melamine based amino-dendrimer - grafted mesoporous siliceous foam. Grafting by up to fourth generation melamine dendrimer resulted in a CO<sub>2</sub> capacity of 0.87 mmol g<sup>-1</sup> at 25 °C, while the increase in enthalpy of adsorption supported that chemisorption is the main mechanism of sorption mainly through primary amines. Interestingly, the aforementioned functionalization was found to enhance the thermal stability of the adsorbent as well.

Functionalization of mesoporous SBA-15 by amino dendrimers based on acrylate as well as melamine was reported by Jing et al. (Jing et al., 2014). The authors carried out propylamine pretreatment of mesoporous SBA-15, followed by introduction of acrylate- as well as melamine amino-dendrimers via a step growth mechanism. In the resulting functionalized adsorbents, primary amines offered major contribution to CO<sub>2</sub> adsorption compared to secondary and tertiary ones. Fixed bed CO<sub>2</sub> adsorption studies at 30 °C revealed capacities of 0.45, 0.46, 0.54, and 0.38 mmol g<sup>-1</sup> for dendrimers of acrylate ethylenediamine, melamine ethylenediamine, melamine diethylenetriamine, and melamine triethylenetetramine, respectively. Excluding few compositions, the capacity of these dendrimer - functionalized SBA-15 adsorbents was found to decrease with increasing temperature from 30 to 75 °C. The performance for amino dendrimer - based CO<sub>2</sub> adsorbents is summarized in Table 4.

According to above studies, the highest capture capacity of 1.82 mmol g<sup>-1</sup> (Bhagiyalakshmi et al., 2010) is noticed for SBA-15 supported generation 3 tris(2-aminoethyl)amine dendrimer CO<sub>2</sub> sorbent. The important challenge associated with this class of sorbent materials is to optimize the performance by effective selection of starting materials and tuning of dendrimer generation. More efforts

needs to be dedicated for supported dendrimer - based CO<sub>2</sub> sorbents synthesis in order to build upon the observed potential and overcome associated challenges, e.g. with respect to cost of dendrimer systems.

## 7. Hyperbranched polyamine – based adsorbents

Hyperbranched polymers constitute irregularly ordered 3-dimensional macromolecular dendritic polymer structures featuring extreme branching density and functional groups of both linear and terminal units (Table 1) (Gao and Yan, 2004; Zheng et al., 2015). Hyperbranched polyamines, an attractive subcategory of hyperbranched polymers, have been reported for applications related to CO<sub>2</sub> capture mainly owing to their increased amine or nitrogen density (Chaikittisilp et al., 2013; He et al., 2016; Yang et al., 2010a). Herein, we overview works on hyperbranched polyamine - based adsorbents for CO<sub>2</sub> capture.

A hyperbranched polyamine solid adsorbent was explored by He et al. (He et al., 2016). For the preparation of the hyperbranched polyamine, amine and methyl acrylate were first treated via the Michael addition route at 0 °C and subsequent self-condensation at 100 and 140 °C for 2 h each, followed by glutaraldehyde-induced cross-linking. In order to prepare a CO<sub>2</sub>-imprinted version, a CO<sub>2</sub> pre-adsorption step was included in the aforesaid synthesis route. The latter form was found to exhibit higher CO<sub>2</sub> capacity and amine efficiency due to its porous nature. Interestingly, additional NaBH<sub>4</sub> - induced reduction treatment had a positive effect to the CO<sub>2</sub>-imprinted version through the conversion of imino groups into secondary amines. Accordingly, a CO<sub>2</sub> capacity of 7.65 mmol g<sup>-1</sup> was obtained for the reduced CO<sub>2</sub>-imprinted version of hyperbranched polyamine based on tetraethylenepentamine at 20 °C in 10 % CO<sub>2</sub> and humid conditions, as compared to triethylenetetramine and diethylenetriamine - based systems having adsorption capacities of 6.72 and 5.78 mmol g<sup>-1</sup>, respectively.

Drese et al. (Drese et al., 2009) reported the preparation of a CO<sub>2</sub> adsorbent - based on hyperbranched aminosilica. For the preparation of the adsorbent, aziridine was polymerized on an SBA-15 support by ring opening means in the presence of glacial acetic acid. Among the various amine loadings, an optimum CO<sub>2</sub> adsorption capacity of 5.6 mmol g<sup>-1</sup> was received for the adsorbent with 10 mmol N g<sup>-1</sup> amine loading at 25 °C in a humid 10 % CO<sub>2</sub>/Ar mixture. In another study, hyperbranched aminosilica via vapor-phase transport means was explored (Chaikittisilp et al., 2013) and was found to maintain a good cyclic stability and an adsorption capacity of 0.93 mmol g<sup>-1</sup> at 25 °C.

Grafting of hyperbranched polyamine into polypropylene fibers bearing acrylamide functionalities via reaction of pentaethylenehexamine and acrylamide was reported by He et al. (He et al., 2017). The resulting 3-dimensional porous system exhibited a CO<sub>2</sub> capture capacity of ca. 5.64 mmol g<sup>-1</sup> in humid 10 % CO<sub>2</sub>/N<sub>2</sub> mixture at 25 °C. An appreciable amine efficiency of 88.2 % was observed as well for such adsorbent along with enhanced regenerability. Table 4 displays the summary of the studies related to hyperbranched polyamine - based CO<sub>2</sub> adsorbent systems.

From the available reports, it can be noted that hyperbranched polyamine - based CO<sub>2</sub> sorbents exhibit high potential, whereas precise attention has to be dedicated on the selection of polymerization technique. For example, a capture capacity of 5.6 mmol g<sup>-1</sup> (Drese et al., 2009) is reported for ring opening polymerized aziridine - based hyperbranched polyamine on SBA-15. Apart from that, a capture capacity of 5.64 mmol g<sup>-1</sup> (He et al., 2017) is noted for hyperbranched polyamine generated via Michael addition on acrylamide - functionalized polypropylene fibers. The influence of starting materials as well as synthesis approach on the performance of hyperbranched polyamine CO<sub>2</sub> sorbents and the connection with stability over cyclic operations need to be more systematically explored.

## 8. Conclusions and future directions

Efforts are being intensified to capture emitted CO<sub>2</sub> from more and more possible industrial sources, including those having low concentrations and/or involving mixtures with challenging constituents, e.g. toxic, competitive with respect to capture etc. In the field of adsorption, which is considered as one of the most attractive energy-efficient alternatives to classical solution-based absorption technology, a plethora of novel materials are being discovered and explored, yet a platform of suitable materials/systems to treat a wide range of industrial emissions at large scale still remains a challenge. The reason is that multiple factors need to be met at the same time, i.e. adsorbents need to exhibit (A) high capacity, selectivity, fast kinetics, and low energy consumption, and (B) chemical and thermal stability, sustainable performance for many cycles, low manufacturing cost, and mechanical robustness at large scale.

This challenge is being battled through the development of robust materials that meet the criteria in category (B) and are modified/functionalized/hybridized at molecular precision and order to encounter the required characteristics so that they also meet the criteria in category (A). Innovative combinations of controlled organization of one or more types of polyamines on surfaces together with formation of multifunctional porous hybrid scaffolds has a high potential of bringing this realization closer. Polymeric amines such as PEI, PPI, PAA, polyaniline, amino dendrimers, and hyperbranched polyamines on various types of solid supports have been explored at various temperature and pressure conditions, including low partial pressures, and wet conditions. The majority of research attempts focus on the PEI based systems, as PEI exhibits high amine density and content of primary amine chain ends, availability, relatively low cost, and sufficient thermal stability up to ~90 °C. In addition, it exhibits compatibility with a wide range of supports, thus positive effect on capture have been achieved when PEI is combined with supports such as siliceous materials (SBA-15, MCM-41, fumed silica, precipitated silica, mesoporous siliceous foam, silica gel, and other siliceous materials), clays, carbonaceous materials (GO, graphene, CNTs, fullerene, activated carbon, carbon sphere), alumina, MOFs, zeolites, and porous polymers. Diffusion limitations, control of amine type and density, leaching of amine functionalities that affects cyclability, particularly with the impregnated systems, and low oxidative resistance caused by the influence of secondary-primary amine pairs are challenges that need to be systematically explored as to further advance the applicability of these systems. Regarding the latter, PPI has been explored as it exhibits close structural relation with PEI, thus enhancing capture performance, while providing higher oxidative stability, yet difficulties associated to monomer synthesis and polymerization duration often limit its commercialization potential.

PAA brings advantages with respect to oxidative resistance and resistance to thermal stresses, while it exhibits stronger intermolecular cohesive forces and adhesive forces with the surfaces to be functionalized, thus offering enhanced binding strength to supports. In comparison to the PEI-based systems, supported PAA adsorbents often displays improved performance with respect to many performance indicators. Polyaniline offers analogous benefits, which are combined with the easiness of synthesis, high thermal stability, and availability in nanostructured forms with large surface areas. Based on the comparative results and potential, PAA- and polyaniline-based adsorbents and related capture processes are particularly worth to be further and more systematically explored. Highly beneficial functionalization has also resulted from dendritic polymers, such as amino dendrimers and hyperbranched polyamines, owing to their high amine/nitrogen density and unique morphological features. From comparison based on the up-to-date reports, hyperbranched polyamines appear more favorable with respect to capture performance. From a process integration point of view, various adsorption process modes can be employed to optimally utilize polyamine-functionalized adsorbents, such as temperature swing adsorption (TSA), pressure and/or vacuum swing adsorption (PSA,

VSA, or PVSA, TVSA, TPSA), moisture swing adsorption (MSA), etc. It is anticipated however that thermal energy needs to be involved as chemical interactions of CO<sub>2</sub> with the amine surface functionalities dominate the capture. As such a hybrid model of TPSA for instance may work more favorably.

Conclusively, research on polyamine-functionalized robust porous adsorbents for CO<sub>2</sub> capture needs to be enhanced as these systems entail high potential to overcome current barriers that hinder industrial realization of carbon capture adsorbents. In many studies, adsorption capacity is justifiably the main performance criterion as it is a key parameter which decides the applicability of the developed systems and the main reason for performing such functionalization. Yet, other parameters including kinetics, stability, regenerability, heat of adsorption, and selectivity also are of crucial importance, and the research community needs to expand the studies to include systematic evaluation of these critical parameters as well. Controlled grafting technologies need to be further developed by parametrically altering amine type, content, and linker to the supports per macromolecule, and functionalization conditions and parameters, as to ensure stability and sustainable performance, tune effects of locality, spacing, orientation, and interconnectivity of the functionalities, and minimize diffusion limitations while maximizing capture and release performance. A great prospect also lies in proper pre-modification of the supports, for example, employing advanced techniques such as UV treatment (Varghese et al., 2020). In the front of functionalization evaluation, the efficiency of the functionalization needs to be assessed in more detailed. To this extent, *in situ* techniques are suggested to be employed. For instance, *in situ* Raman and FTIR in the presence of CO<sub>2</sub> and/or other competing gases/vapors, such as N<sub>2</sub>, CH<sub>4</sub> and humidity, at various pressures and temperatures during both adsorption and desorption are recommended. In fact, *in situ* spectroscopy analysis in the presence of the gases at the P, T conditions of a simulated process can shed light on the mechanisms and interactions of the gases with the adsorbents and the amine surface functionalities, and provide valuable feedback in order to further optimize the developed systems as to achieve the required performance targets. Loading the same adsorbent with more than one type of polyamines and involving composite porous supports consisting of more than one type of material is also suggested as to achieve multifunctionality and meet a wider range of performance indicators, as required for the transition of carbon capture by adsorption to true industrial implementation.

## Declarations of Competing Interest

None.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.ijggc.2020.103005>.

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