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Unveiling host-guest interactions and stability of amine-functionalized silica sorbents for carbon capture

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ABSTRACT

Despite making significant progress in terms of capture kinetics and capacity, the thermochemical and cyclic instability of silica-based amine functionalized adsorbents present challenges for their practical implementation and economic viability. Accordingly, this work provides a critical review to analyse factors affecting thermal and cyclic stability of functional silica-based sorbents. The first section provides background information and context for the review. The second section focuses on the synthesis routes employed for silica-based amine functionalized adsorbents. The third section delves into the mechanism underlying the thermal and cyclic instability observed in these adsorbents. The fourth section explored the factors that influence the thermal and cyclic stability of silica-based amine functionalized adsorbents. The last section dissects host-guest interaction in silica-based amine functionalized adsorbents. The review concludes by underscoring the importance of further research and development into host-guest interaction studies in amine functionalized adsorbents to optimize performance and address the challenges associated with thermal and cyclic instability, thereby enhancing the practical feasibility of these adsorbents in carbon capture applications.

List of Abbreviations and Nomenclature

Abbreviation/ Nomenclature	Meaning
AFA	Amine Functionalized Adsorbents
AGAs	Amine-Grafted CO_2 Adsorbents
CVD	Chemical Vapor Deposition
DEA	Diethanolamine
DETA	Diethylenetriamine
DGT	Dry Gel Tumbling
EMSNTS	Enhanced Mesoporous Silica Nanotube
EG	Ethylene Glycol
ED	Ethylenediamine
GPAA	Guanidinylated Poly(Allylamine)
HNTS	Halloysite Nanotubes
HMDS	Hexamethyldisilyamine
PE-MCM-41	Pore-Expanded MCM-41 Silica
IPA	Isopro-Panol Amine
MC	Mesoporous Capsule
MDEA	Methyl Diethanolamine
MLD	Molecular Layer Deposition
MEA	Monoethanolamine
TMSP	N- [3- (Trimethoxy Silyl) Propyl]
PEHA	Pentaethylenehexamine
PEG	Polyethylene Glycol
IM	Imidazole
PEI	Polyethyleneimine
PP-GMA-TETA	Polypropylene- Glycidyl Methacrylate-Triethylenetetramine
TEPA	Tetraethylenepentamine
TEA	Triethylamine
T-CVD	Tumbling Chemical Vapor Deposition
2-MI	2-Methylimidazole
APTES	3-Aminopropyltriethoxysilane
APTMS	3-Aminopropyltrimethoxysilane

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1. Introduction

The sixth assessment report of the IPCC asserts that the risk posed to ecosystem integrity, functioning and resilience by climate change is expected to increase with every 0.1 °C increase in global warming and hence recommends a global average warming temperature of 1.5 °C above pre-industrial levels by 2100 to forestall this occurrence [1]. The prominent gas responsible for global warming is identified to be anthropogenic CO_2 emissions [2–6]. Hence, various technologies, including pre-combustion capture, post-combustion capture, oxyfuel combustion, and direct air capture, are being developed to address the impact of anthropogenic CO_2 emissions. Amine scrubbing, a commonly used method, faces challenges such as high energy consumption and equipment corrosion, prompting interest in physisorbent like activated carbon, zeolite, silica, and metal-organic frameworks (MOFs) for efficient gas separation. Generally, Solid amine adsorbents solid sorbents adsorb CO_2 through physical interaction (physisorption), or a chemical bonding between the adsorbate and adsorbent surface (chemisorption). Physisorption is influenced by factors such as surface energy, pore sizes, pressure and temperature at the adsorption site [7,8]. Accordingly, at high pressure and low temperature, adsorption sites with higher surface energies and suitable pore sizes will promote the adsorption of targeted molecules. In chemisorption, adsorption occurs through chemical bonding between the gas molecules and functional molecules within the adsorbent matrix [9,10]. Functionalizing adsorbents with amines enhance their capacity and selectivity for CO_2 capture compared to non-functionalized adsorbents, where physisorption is the primary adsorption mechanism. Amine-functionalized silica adsorbents have emerged as highly effective materials for carbon capture, especially in post-combustion processes where capturing low concentrations of CO_2 from flue gases is critical. Their effectiveness stems from the combination of silica's high surface area [11] and the chemical affinity of amine groups for CO_2 molecules [12–22], which allows for efficient adsorption even at low partial pressures. By functionalizing silica surfaces with amines, these adsorbents exhibit enhanced CO_2 capture capacity and selectivity over other gases, making them suitable for large-scale applications. Additionally, silica is thermally stable upto 800 °C [23], has a tuneable pore structure [24], and is relatively easy to functionalise [25], which provides flexibility for tailoring materials for various adsorption requirements. As a result, amine-functionalized silica adsorbents are a promising solution for industrial carbon capture applications aimed at reducing greenhouse gas emissions and mitigating climate change. However, the advancement in selectivity and capture capacity through using highly amine functionalized adsorbents often come with attendant consequence of high isosteric heat of adsorption [26,27]. The isosteric heat of adsorption is a critical parameter in evaluating the efficiency and durability of adsorbents, particularly in carbon capture applications [28]. In the case of amine-functionalized silica adsorbents, higher isosteric heat of adsorption implies that more energy is released when CO_2 molecules bind to the amine groups [10,29]. While this enhances the initial capture efficiency, it also brings about significant thermal stress on the adsorbent material during each adsorption-desorption cycle [30]. This thermal stress causes a gradual degradation of the amine groups embedded within the silica matrix, as they undergo repeated heating during regeneration. Over time, these high-temperature cycles lead to the breakdown or volatilization of the amine groups, reducing their effectiveness and resulting in a progressive decline in the adsorbent's CO_2 capture capacity [31]. Consequently, while highly amine-functionalized silica adsorbents offer significant advantages in terms of selectivity and capture capacity, their elevated isosteric heat of adsorption and the resulting cyclic instability undermine their long-term commercial viability. Research is, therefore, focused on balancing capture performance with thermal and cyclic stability to create adsorbents that can endure the rigorous demands of industrial carbon capture operations. There have been extensive reviews in this area, as tabulated in Table 1. Prominent in these reviews are the contributions of Jahandar

Table 1
Summary of literature reviews relating to thermal and cyclic stability of amine functionalized adsorbents.

Source	Date	Scope of Review
Fan et al. [33]	2022	This review offers a comprehensive overview of the roles played by the support material and amine structure in improving the CO_2 adsorption performance and stability of solid adsorbents. It also explores recent advancements in reactor design specifically optimized for solid amine adsorbents, providing valuable insights into the development of continuous CO_2 capture processes for efficient separation from both flue gas and ambient air.
Yamada [35]	2021	This review delves into CO_2 capture technologies at large-scale CCS facilities such as use of CO_2 sorbents and solvent, focusing on amine-CO_2 reactions in amine sorbents and their impact on separation efficiency. The review projects amine-based methods are seen as key to accelerating CCUS deployment due to their efficiency and reliability. The review also addressed challenges like amine degradation, emissions, and environmental impacts, extending to polymers.
Fatima et al. [36]	2021	This review examines the development and advancements of functionalized silica-based adsorbents for CO_2 capture, focusing on surface modification techniques, the interaction mechanisms involved in CO_2 adsorption, and the impact of moisture on adsorption performance.
Cherevotan et al. [37]	2021	This review delves into literature concerning the chemical interaction between CO_2 and sorbents, with a focus on inert porous silica immobilized amine materials. It distinguishes these materials from others like metal hydroxides and amine solutions. Discussions include advantages, CO_2 capture mechanisms, desorption, regeneration, degradation pathways, and sustainability of amine-functionalized silica materials.
Zhao et al. [38]	2021	This review focuses on recent advancements in amine-functionalized solid adsorbents, which are synthesized using a variety of supporting materials such as mesoporous silica, zeolites, porous carbon materials, metal-organic frameworks (MOFs), and composite porous materials derived from waste sources.
Sharma and Dhir [4]	2021	This review examines the essential qualities of solid adsorbents for CO2 capture, including CO2 selectivity, adsorption capacity, mechanical strength, thermal stability, moisture resistance, reusability, cost-effectiveness, and ease of regeneration, for both carbonaceous and non-carbonaceous materials.
Varghese et al. [39]	2020	This review focuses on recent advancements in polymeric amine-functionalized solid adsorbents for CO2 capture, evaluating research on various polymers. By comparing these systems, the review identifies optimal approaches and highlights emerging trends and future directions in the development of effective CO2 capture technologies.
Gelles et al. [40]	2020	The review delves into the advancements in developing amine-based CO_2 capture adsorbents, emphasizing material development and evaluation progress. It explores criteria for evaluating these adsorbents, including CO_2 working capacities, selectivity, adsorbent stabilities, sorption kinetics, and minimizing overall energy demands.
Zhang et al. [41]	2019	This review summarized advancements in amine-modified silica for CO_2 capture over the past two years. It explores their preparation methods and performance characteristics in capturing CO_2.
Jahandar Lashaki et al. [32]	2019	This review examines the physical and chemical properties of adsorbents, the composition and characteristics of the feed gas, and the operational parameters of adsorption–desorption processes in relation to the long-term stability of amine-functionalized CO_2 adsorbents. It also addresses adsorbent degradation resulting from exposure to

(*continued on next page*)

Table 1 (*continued*)

Source	Date	Scope of Review
		high temperatures, oxygen, dry CO_2, sulphur compounds, nitrogen oxides, and steam.
Yu et al. [42]	2018	This review discussed progress in developing amine-functionalized silica/organosilica membranes including comparison of various organosilica membranes with either unhindered or sterically hindered amines.
Darunte et al. [12]	2016	This review highlighted the developments in the utilization of solid-supported amines for carbon dioxide (CO_2) capture with emphasis on the performance of amine-functionalized metal organic framework (MOF) materials in capturing CO_2 under humid conditions and their ease of regeneration. It also discussed various regeneration techniques, such as temperature swing in a CO_2 purge stream and temperature swing through steam stripping. Additionally, the article discusses emerging methods for gas-solid contacting that can enhance CO_2 capture using amine adsorbents.
Yu et al. [43]	2012	In this review, the selection of adsorbent is compared and discussed based on major concerns for selection of adsorbent, such as cost, adsorption rate, CO_2 adsorption capacity, and thermal stability.
Samanta et al. [44]	2012	The review examines various promising sorbents, including activated carbonaceous materials, silica or zeolites with microporous/mesoporous structures, carbonates, and polymeric resins, for CO_2 removal from flue gas streams. It discusses different methods of enhancing sorbent performance through impregnation of functional groups and modification of support materials, evaluating attributes such as adsorption/desorption kinetics, regeneration, equilibrium adsorption capacity, durability, and selectivity.

Lashaki et al. [32], Fan et al. [33] and Hack et al. [34]. Jahandar Lashaki et al. [32] who elaborately discusses the stability of adsorbents in terms of thermal, hydrothermal, and chemical stability as a critical factor that influences the lifetime and operational costs of CO_2 capture. Fan et al. [33] work provided a comprehensive summary of recent research, with a particular emphasis on the crucial roles played by support materials and the structural characteristics of amines in enhancing CO_2 adsorption performance and overall stability. Concurrently, Hack et al. [34] provided an overview of mechanistic studies on CO_2 adsorption.

This review complements the literature by delineating advancements in enhancing the thermal and cyclic stabilities of amine-functionalized adsorbents (AFA), identifying influencing factors, and elucidating the effects of impurities on silica-based AFA. Additionally, it delves into mechanistic studies on host-guest interactions in AFA, proposing avenues for leveraging this knowledge to enhance thermal and cyclic stability and outlining both opportunities and challenges for future research.

Accordingly, this review is organized into six sections. Section 1 introduces the topic. Section 2 discusses the methods of functionalizing adsorbents with amines. Section 3 focuses on the mechanism responsible for thermal and cyclic instability. In section 4, the factors that enhance the thermal and cyclic stability of AFA and the effect of impurities on the stability of AFA during operation are discussed. Section 5 dissects host-guest interaction in silica-based amine functionalized adsorbents. Finally, section 6 draws the review to a conclusion.

2. Preparation of amine functionalized adsorbents

Understanding the functionalization of adsorbents with amines is important for designing high-performance materials that can effectively capture gases while maintaining long-term stability and sustainability. This research plays a key role in optimizing adsorbent materials for use in climate change mitigation technologies and environmental protection. Solid amine adsorbents have been of interest as materials for CO_2 capture because of the following qualities: strong affinity for CO_2 which aids CO_2 selectivity and capture capacity [29,45,46], lower corrosion effect on equipment and fugitive emissions [12,47–49], and lower energy requirement during regenerative cycle when compared with aqueous amine [50]. AFA can be formed by three main processes, namely impregnation, tethering or grafting, and in-situ co-condensation. Impregnated amine adsorbents can be developed by physical interaction of amines on the surface of the support [51]. In a typical impregnation process, the specified amount of amine is initially dissolved in methanol with continuous stirring for around 15 min. Subsequently, the silica material targeted for functionalization is added to the solution, generally maintaining a silica-to-methanol weight ratio of 1:8. The resulting slurry is then stirred for an additional 30 min and dried at 70 °C under a vacuum of 700 mmHg for 16 h. [25,52,53]. Fig. 1 illustrates the standard procedure for impregnation method. In this procedure, the amine molecules become physically attach to the support surface due to the van der Waals force and hydrogen bonds between the amine and the silica support. Impregnation is best achieved by using amino polymers with large chains which produce large van der Waals's forces that aid in retaining the amine in the pores, thereby enhancing cyclic retention [40]. When amine with shorter moieties, such as pentaeth-ylenehexamine (PEHA), diethanolamine (DEA), methyl diethanolamine (MDEA), tetraethylenepentamine (TEPA), mono-ethanolamine (MEA), ethylenediamine (ED), isopro-panol amine (IPA), diethylenetriamine (DETA) are used for impregnation, the resulting AFA exhibit higher cyclic leaching because of reduced van der Waals' adhesion [54–56]. Researchers including Wang et al., [54,57–60] used polyethyleneimine (PEI) which is a large amino polymer to form silica, zeolite, and MOF type of AFA using the impregnation method.

Silane tethering is achieved by a covalent grafting of amine to the organosilane at the target surface, causing multiple covalent bonds per amine centre to exist within the adsorbent matrix [29,40,48,61]. The standard grafting procedure, as illustrated in Fig. 2, begins with drying the sample requiring functionalization at a temperature range of 110 °C–150 °C under vacuum (40 mbar) for 3 h to eliminate any residual moisture, thereby reducing the potential for polymerization of silane branches during grafting. After cooling, the system is purged with nitrogen to establish an inert environment and prepared for reflux. Toluene is then added to the flask containing the sample designated for functionalization. Following this, a precise amount of amino organosilane is introduced, and the mixture is heated to a temperature range of 70 °C–85 °C for 12–18 h under reflux conditions. Once grafting is completed, the sample is filtered under vacuum suction and thoroughly rinsed with an excess of toluene and methanol to remove any unreacted residues. Finally, the sample is vacuum dried for 6 h at 50 °C to ensure complete removal of solvents and bond stability [29,62,63].

Short chain amines like pentaethylenehexamine (PEHA), diethanolamine (DEA), methylethanolamine (MEA), triethylenetetramine (TETA) are favoured in formulation of AFA through silane tethering because of their lower energy requirement which aid tethering process [48,65,66]. Amino silanes like 3-Aminopropyltrimethoxysilane (APTMS) and 3-Aminopropyltriethoxysilane (APTES) also serve as silane tethering agents because of their reactive amino group (NH_2), which readily reacts with various functional groups on surfaces, including hydroxyl (-OH) groups found on silica and other oxide surfaces. This reaction between the akyl group of the aminosilane and the surface hydroxyl groups results in the formation of stable siloxane bonds (-*Si*-*O*-Si-), firmly anchoring the silane molecule to the surface [63,67,68].

The in-situ co-condensation method of forming AFA is achieved when amine containing monomers undergo polymerization. In this approach, the amine-functionalizing agent, such as APTES, is added alongside the silica source, typically tetraethyl orthosilicate (TEOS), and a pore-directing agent (surfactant) during the synthesis of silica sample. The pore-directing agent (like cetyltrimethylammonium bromide, CTAB) helps form the mesoporous structure by self-assembling into

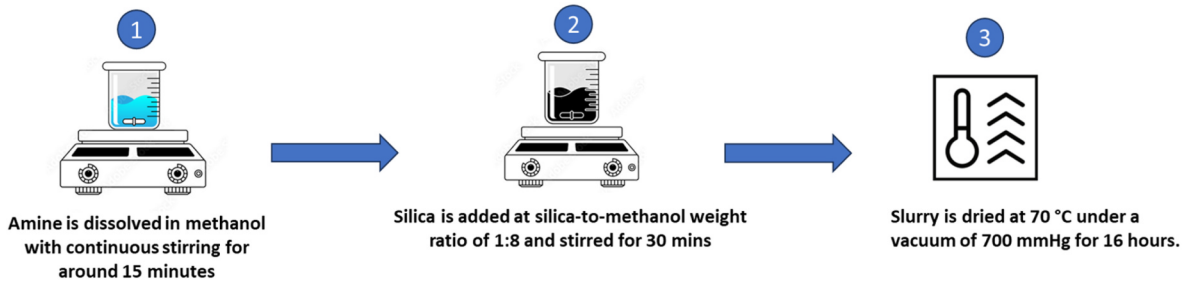

Fig. 1. Impregnation procedure.

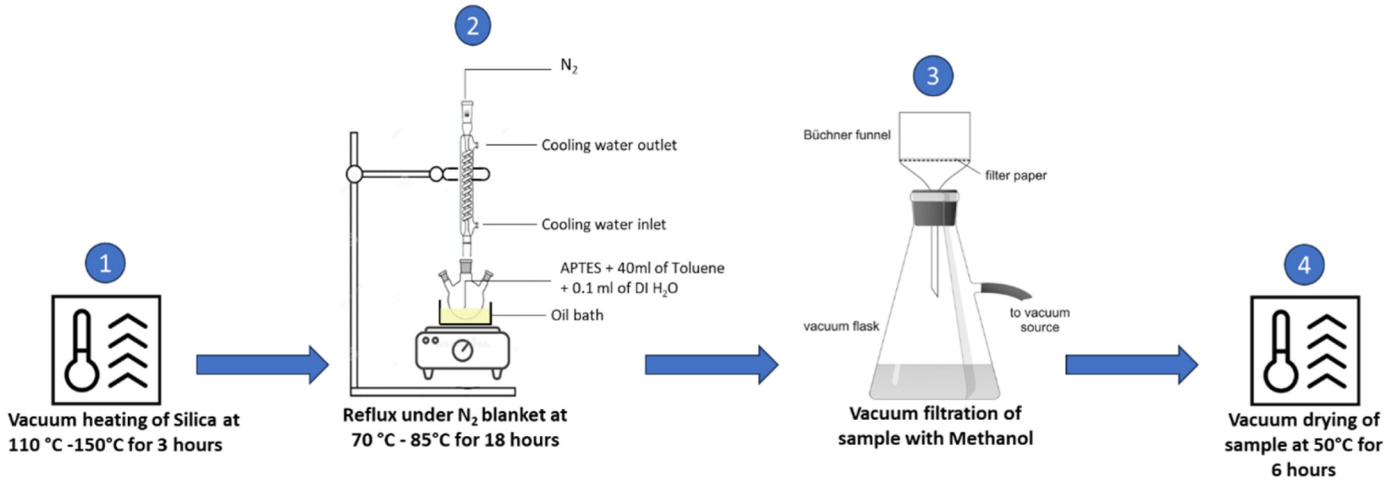

Fig. 2. Illustration of grafting procedure.

micelles, which create a template for the silica network. The TEOS and functionalizing agent undergo hydrolysis and condensation together, creating a covalent incorporation of the amine groups directly within the silica framework as seen in Fig. 3 [64]. This method distributes amine groups throughout the entire silica matrix instead of just on the surface.

Functionalizing an adsorbent typically reduces its pore diameter and introduces steric hindrance, which can impede the chemisorption mechanism, especially in microporous sorbents [69]. The pore sizes in nanoporous materials, which serve as host matrices or solid supports during amine functionalization of adsorbents, are generally classified as microporous (less than 2 nm), mesoporous (between 2 nm and 50 nm), and macroporous (greater than 50 nm) [70,71]. Among these categories, mesoporous materials have proven to be particularly suitable for both physisorption and chemisorption. The mesopores facilitate the attachment of amine groups to the support structure with minimal steric hindrance, allowing more efficient CO_2 capture mechanisms [58, 71–76].

Silica, one of the most prominent mesoporous supports, has garnered significant attention in the study of CO_2 adsorption due to its unique structural characteristics. For instance, in a study conducted by Ahsan et al. [77] aimed at comparing the cyclic adsorption-desorption of CO_2 of zeolite-5A molecular sieves and amine-grafted SBA-15 in enclosed environments using a mixture of 1 % CO_2 in N_2. It was observed that although AFA achieved similar equilibrium CO_2 uptake and cyclic performance stability, the amino silica material performed better than the zeolite-5A material by (i) utilizing a lower activation and regeneration temperatures, (ii) possessing shorter activation and regeneration durations, and (iii) achieving faster CO_2 adsorption kinetics. Furthermore, attributes such as a large surface area, well-organized mesoporous structure, high pore volume, thermal stability, and tolerance to impurities make these sorbents highly advantageous [78] contributing to their widespread acceptance and utilization in CO_2 capture studies.

3. Mechanisms of thermal and cyclic instability in silica-based amine functionalized adsorbents

The mechanisms responsible for thermal and cyclic instability in silica-based amine functionalized adsorbents can be intricate and multifaceted. Generally, thermal instability arises from loss of functionality in the sorbent due to significant degradation or structural changes at high temperature, while cyclic instability occurs when the adsorbent loses its capacity for CO_2 capture over successive cycles. Key mechanisms that contribute to thermal and cyclic instability discussed in this section include amine and silica degradation, moisture sensitivity, type of support structure, chemisorbed species formation and amine type and functionalization method.

3.1. Amine and silica degradation

One of the earliest studies on the thermal and cyclical stability of AFA was conducted by Xu et al., [52] were MCM-41 was hydrothermally synthesized from a mixture with $50SiO_2$:$4.32Na_2O$:$2.19(TMA)_2O$:15.62 (CTMA)BR:$3165H_2O$ and impregnated with 50 wt% PEI. In the study, it was observed that pure PEI losses 3.8 % of its weight at 100 °C; begins to decompose at 150 °C with a sharp weight loss at 205 °C and finally decomposes at 600 °C. However, when immobilized in MCM-41, it was observed that the decomposition temperature reduced to 125 °C causing a 10.5 % weight loss of the AFA at 100 °C as shown in Fig. 4.

This implies that immobilized PEI became thermally unstable at a temperature lower than the decomposition temperature of pure PEI and began to decompose after 7 cycles when operated at 75 °C. Xu et al., [52] ascribed the decrease in the PEI decomposition temperature to its volatility causing it to spread through the host sorbent pores, thereby

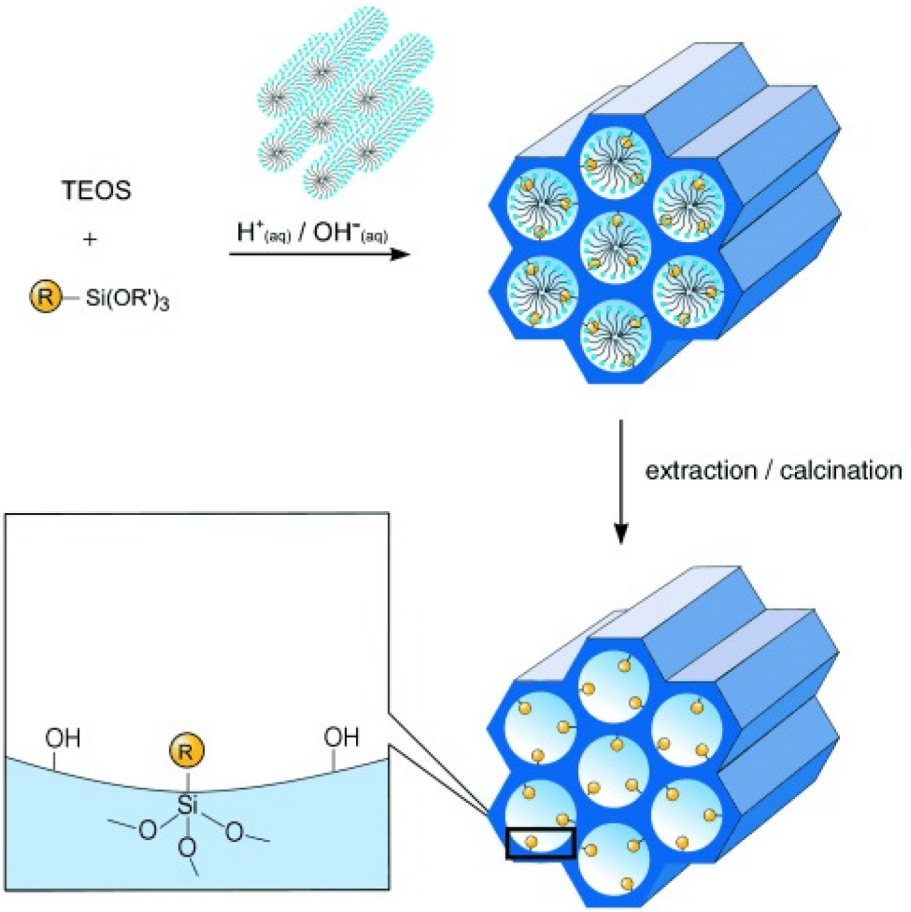

Fig. 3. Illustration on In-situ co-condensation procedure [64].

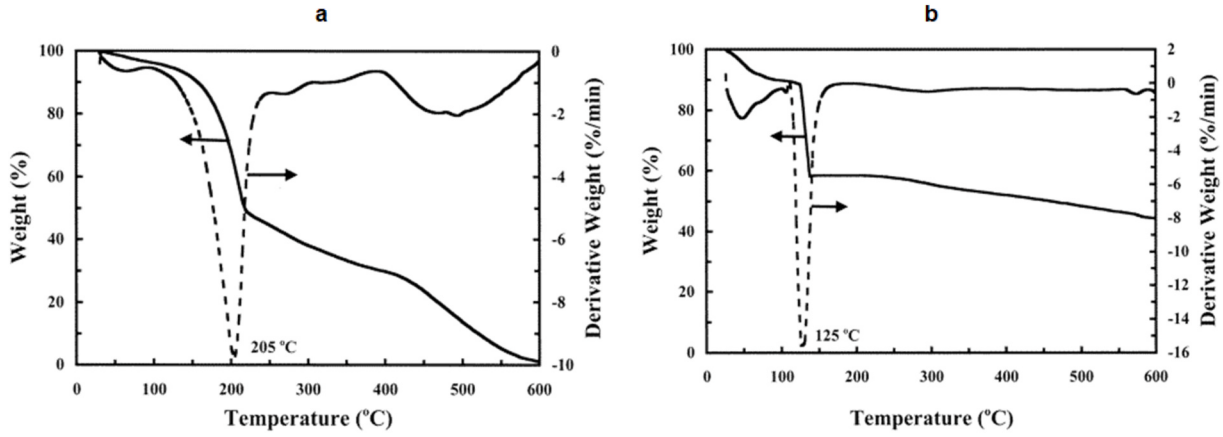

Fig. 4. (a) TGA profile of pure PEI (b) TGA profile for MCM-41-PEI-50 [52].

decreasing its size and consequently its decomposition temperature. Following the outcome of the study by Xu et al., [52], Franchi et al., [79] developed an AFA by impregnating pore-expanded MCM-41 silica (PE-MCM-41) with DEA. The increased pore sizes of PE-MCM-41 facilitated higher DEA loading, resulting in enhanced CO_2 adsorption. However, during operation at 75 °C for adsorption and 100 °C for desorption, a 3.3 % reduction in CO_2 uptake was observed. Additionally, after 7 cycles, deterioration of the AFA was evident. The reduced CO_2 uptake was attributed to DEA loss caused by mass loss in PE-MCM-41 at the desorption temperature, indicating silica degradation in PE-MCM-41. Franchi et al., [79] suggested that the use of polyethylene glycol (PEG) could reduce the thermal instability observed based on an earlier work carried out by Satyapal et al., [80] where it was reported that PEG can improve thermal stability due to its ability to attract more water to the surface of the support due to the hygroscopic nature of the chemical and probably due to the preponderance of OH^- ions from the polyethylene glycol molecules. Outcome of the studies by Xu et al., [52] and Franchi et al., [79] show that thermal and cyclic stability can be affected by amine and silica degradation. Niu et al., [81] carried out a study aimed to develop an emerging nanocomposite for capturing CO_2. Mesoporous silica nanocomposite tube was impregnated with 50 wt% PEI (MP– 50) and subjected to adsorption – desorption cycles at 60 °C

and 110 °C, respectively. The AFA recorded peak adsorption capacity of 2.75 mmol/g at 85 °C and becomes thermally unstable when heated to 200 °C and completely decomposes above 400 °C due to degradation/decomposition of PEI chains (Fig. 5a). However, operating within the adsorption–desorption cycle temperature, it became thermally unstable and began to decompose after 10 cycles (Fig. 5b).

Alkhabbaz et al., [82] on mesoporous silica functionalized with Guanidinylated poly(allylamine) (GPAA) for CO_2 capture from flue gas. In the study, PAA and GPAA were used to functionalise silica MCF and then evaluated for CO_2 capture, thermal and cyclic stability capacities. The results revealed that PAA impregnated adsorbents showed better capture capacity at lower amine loadings and capture CO_2 better than GPAA at temperatures lower than 75 °C. GPAA showed better thermal and cyclic stabilities than PAA, and higher CO_2 capture capacities at temperature above 75 C, and approximately 70 % higher capture capacity than PAA at 140 °C. While analysing this observation on the difference in thermal and cyclic stability between PAA and GPAA, Alkhabbaz et al. [82] compared the IR spectra of fresh PAA impregnated MCF to the IR spectra of PAA impregnated MCF after CO_2 adsorption at 140 °C.

The comparison results as seen in Fig. 6 revealed no significant difference in the spectrum and the absence of urea formation. Consequently, the study concluded that the decline in CO_2 uptake and thermal instability of PAA were primarily attributed to amine degradation or polymer conformation rearrangement at higher temperatures rather than the previously presumed formation of urea.

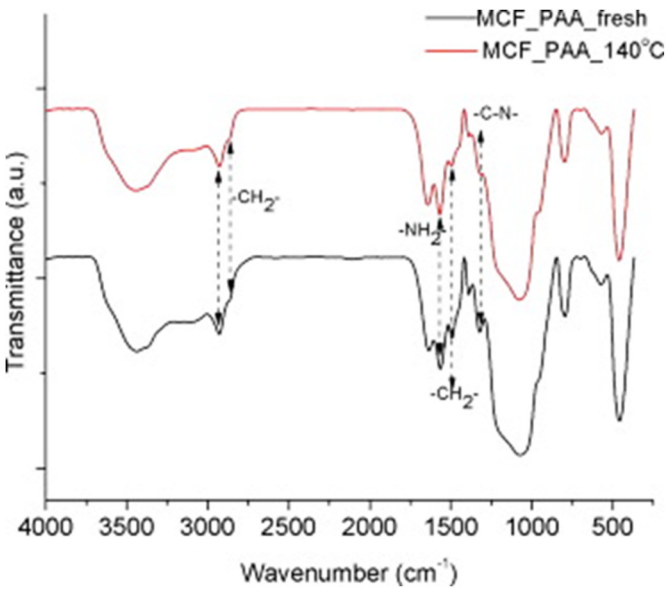

Fig. 6. IR spectra of the fresh MCF_PAA_35 and the sorbent exposed to 10 % CO_2 at 140 °C for 3 h [82].

3.2. Moisture sensitivity

Xu et al., [83] while investigating the influence of Moisture on CO_2 Separation from gas mixture by a nanoporous adsorbent based on polyethyleneimine-modified molecular sieve MCM-41 discovered that water molecules improve CO_2 adsorption and PEI functionalized MCM-41 is more thermally stable in the presence of moisture than pure MCM-41. Xu et al., [83] group posited that since PEI is more hydrophilic than MCM-41, in the presence of moisture, water molecules will choose to be adsorbed into PEI. This leads to more adsorption of CO_2 forming bicarbonate from initially formed carbamate in the absence of moisture, thereby protecting the MCM-41 structure. Hence, in the presence of the abundant amine, more water molecules are adsorbed leading to higher capture of CO_2 and impeding the formation of urea in the sorbent. This understanding was exploited by Shen et al., [26] which led to a capture capacity of 133.8 mg/g adsorbent after 50 cycles. Despite the discovery, the cyclic stability of the AFA did not record a great improvement from the studies carried out by Xu et al., [52] and Franchi et al., [79] as structure deterioration set in after 10 cycles, thus indicating that more research needed to be done in the area.

3.3. Type of support structure

In another research aimed at developing sorbents for separation of CO_2 and H_2S from various gas streams, Ma et al., [84] impregnated SBA-15 with 50 wt% PEI resulted in a better sorption performance than the MCM-41 based sorbent and began to decompose after 20 adsorption-desorption cycles at 75 °C and 110 °C, respectively. This improvement in thermal and cyclic stability was attributed to the structure of SBA-15 which improves its thermal stability relative to that of MCM-41. Zhang et al., [85] used commercial silica gel as support, functionalized with 50 wt% PEI due to its advantages of better hydrothermal stability and higher volumetric adsorption when compared with MCMs and SBA-15. While comparing results of PEI/silica gel with PEI/SBA-15, It was noted that PEI/silica gel had 2.6 times higher volumetric adsorption than PEI/SBA-15 and would degrade thermally after 10 cycles of operating at 75 °C and 100 °C, for adsorption and desorption respectively. Proving that PEI functionalized silica gel is less thermally stable than PEI/SBA-15. A study carried out by Yan et al., [86] aimed at investigating the effect surfactant template would have when incorporated into a Mesocellular siliceous foam (MCF) impregnated with PEI revealed that the surfactant template improved the thermal stability of the AFA when compared with AFA samples without the

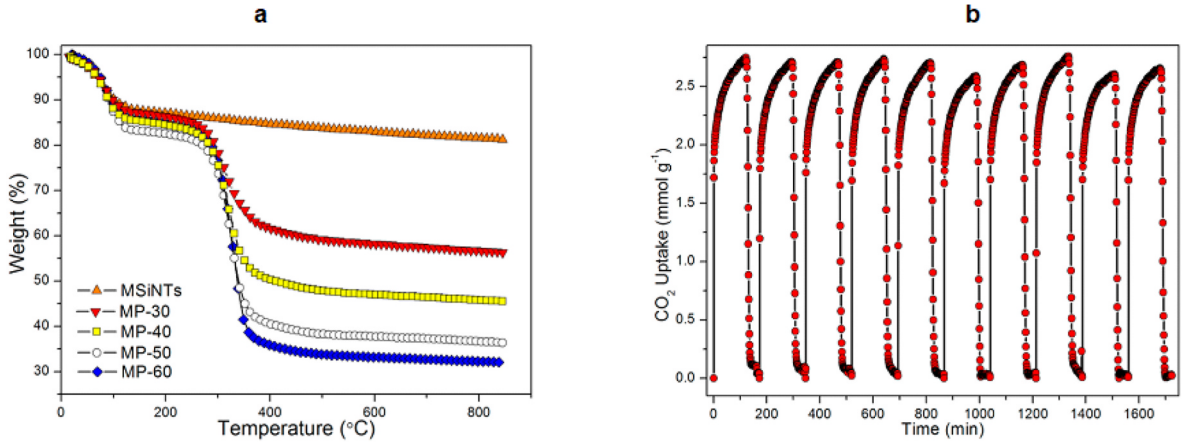

Fig. 5. (a)Thermal stabilities of Mesoporous silica nanocomposite tube at different loadings of PEI, (b) Reversibility test for CO_2 adsorption on MP-50 [81].

surfactant template. The TG and DTG curves in Fig. 7 show that the surfactant templates made of Pluronic (P123) were able to keep the AFA thermally stable and prevent loss of mass up to 250 °C. When functionalized with PEI, it was noted that beyond 250 °C, degradation of the AFA set in hitting its peak at 310 °C which corresponds to the decomposition temperature of P123 and completely decomposed at 390 °C due to final decomposition of the template.

A significant progress towards thermal and cyclic stability of AFA came to light in the research carried out by Qi et al., [87]. In the study [87], a novel mesoporous SiO_2 hollow capsules (having diameter of 400 nm and shell thickness of 10 nm) prepared from TEOS in the presence of a polystyrene latex template were impregnated with 83 wt% PEI and 83 wt% TEPA. This resulted in a mesoporous shell with tuneable thickness grown around the polystyrene particles with the assistance of CTAB acting as mesopore directing agent.

While evaluating the thermal and cyclic stability of the PEI and TEPA functionalized mesoporous capsule (MC) sorbents through temperature swing process where the MC sorbents were exposure to dry CO_2 at 75 °C for 10 min, before increasing the temperature to 100 °C, Qi et al., [87] discovered that both sorbents can be regenerated within 10 min in N_2. As seen in Fig. 8, it was also observed that PEI functionalized adsorbent would begin to degenerate after 50 cycles as it would only retain 88 % of its capacity at 50 cycles, while the TEPA functionalized sorbent which recorded a higher capture capacity begins to degenerate appreciably after 20 cycles and eventually drop to 60 % of its capacity after 50 cycles. This occurrence of better thermal and cyclic stability of PEI MC adsorbent over TEPA MC adsorbent used in the study was attributed to the higher boiling point of PEI, which contributes to better temperature stability.

Also, the improvement seen in the thermal stability could be due to the large pore volume and a thin shell of the MC sorbent, which allowed for the deposition of large percentage of amine [68,88–93]. This is also seen when SBA-15 and PE-MCM-41 were used as sorbents instead of MCM-41 in the works of Ma et al. [84] and Sayari et al. [94], where an increase in capture capacity and thermal stability was recorded (as against use of MCM-41) due to increase in sorbent pore volume.

3.4. Formation of chemisorbed species

In the research conducted by Ref. [95] it was demonstrated that AFA engage in chemisorption reactions with CO_2, resulting in the formation of various products including carbamic acid, carbamate, bicarbonate, and urea as shown in Fig. 9 Carbamate, generated through a zwitterionic mechanism, is identified as the predominant product under water-free conditions and can attach to primary or secondary amine groups, exhibiting notable stability even under vacuum conditions, which

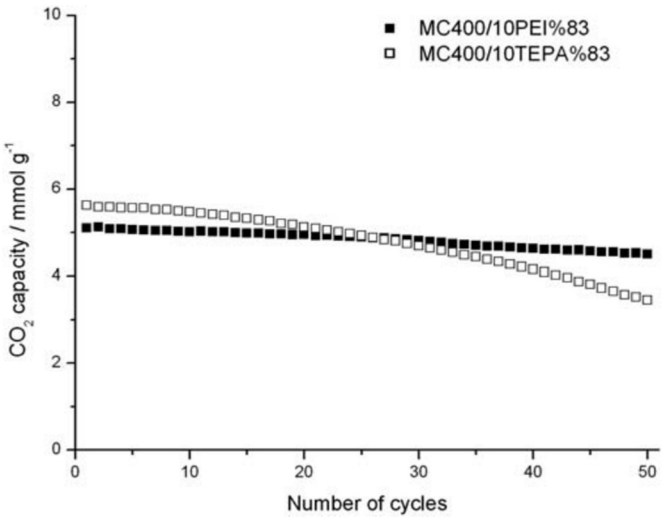

Fig. 8. Cyclic adsorption and desorption of sorbents utilizing mesoporous silica capsules containing 83 % amine employing a temperature swing method [87].

adversely affects cyclic stability. Bicarbonate formation necessitates water, is feasible across various amine types, and occurs at a slower rate than carbamate, with easier reversibility. Upon evacuation, loosely bound chemisorbed CO_2 products like carbamic acid are desorbed.

In a study carried out by Drage et al., [96] on the thermal stability of polyethyleneimine based carbon dioxide adsorbents and its influence on selection of regeneration strategies, 40 wt% PEI was used to functionalise mesoporous silica (KIT-6) via impregnation. The study carried out the adsorption – desorption cycles at 75 °C and 135 °C, respectively. It was observed that PEI impregnated adsorbent increased in mass from 75 °C to 85 °C due to adsorbed CO_2, and then decreases between 95 °C and 135 °C in an atmosphere of air and nitrogen due to adsorbed moisture loss and possibly slow volatilization of PEI occurring at those temperatures. Then, above 135 °C rapid degradation of the adsorbent set in announcing a cyclic failure. This failure at 135 °C in presence of CO_2 was associated to the formation of urea linkages which, as opposed to carbamate formation, is irreversible, leading to irreversible disintegration of the adsorbent as depicted in Fig. 10. Accordingly, the study concluded that thermal regeneration at high temperatures (which leads to thermal stability) of the chemical adsorbent should be a trade-off between efficient regeneration and degradation of the adsorbent.

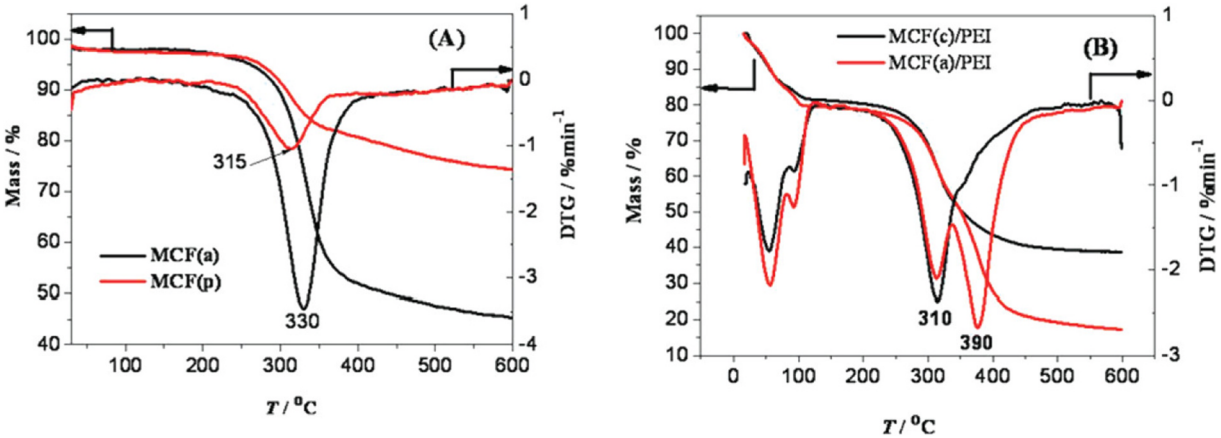

Fig. 7. The TG and DTG curves for **(A)** MCF without template MCF(a), MCF with partial template MCF(p) and **(B)** MCF without template MCF(c)/PEI-50 % and MCF with partial template MCF(a)/PEI-50 % with a temperature ramp of 5 °C/min in pure N_2 [86].

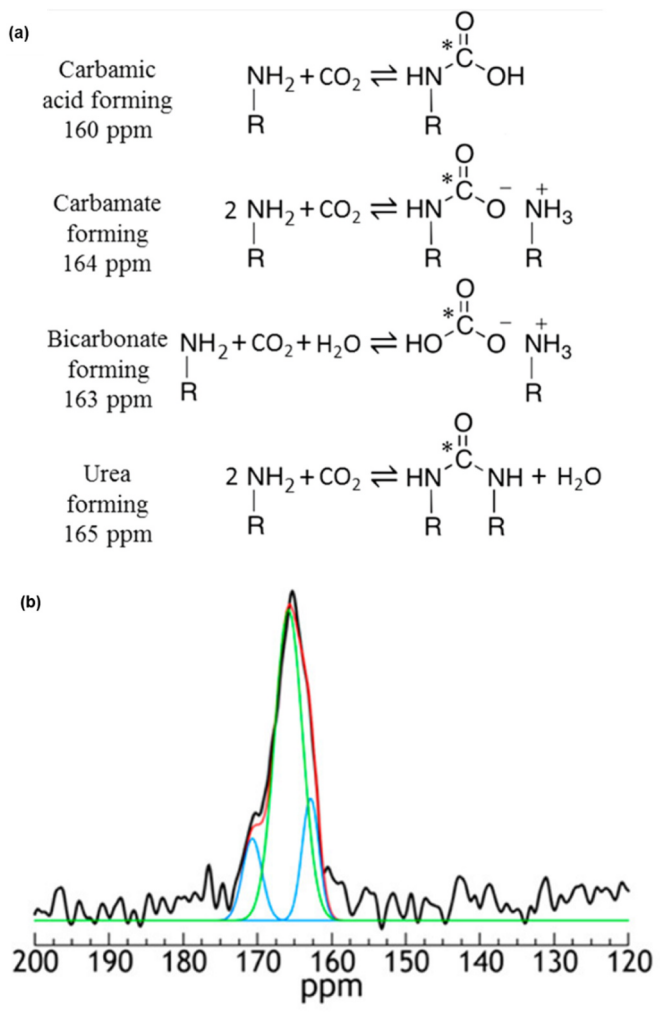

Fig. 9. (a) Reaction pathways of primary amines and CO_2. (b) $^{13}C\{^1H\}$ CPMAS NMR conducted at 3 T on the reacted SBA-15-HAS sample after evacuating it for 31 h [95].

3.5. Amine type and method of functionalization

Ayub et al. [27] while carrying out a study aimed at developing an amine-grafted silica-based sorbent for a single stage biogas upgrading to biomethane grafted 3-aminopropyltrimethoxysilane (APTMS) onto G-10 silica. The choice for APTMS was due to the presence of isolated primary amines in APTMS, which are the most stable amine species in the presence of hot air. Thermo-gravimetric analysis was conducted on the synthesized material to determine the thermal stability of the AFA. The AFA was subjected to a flow of 30 vol% CO_2 in N_2 at 40 °C and was heated till it degraded at 800 °C (heating rate of 10 °C/min) in the presence of N_2. For the cyclic stability test, adsorption was carried out by heating the synthesized AFA in the presence of 30 vol% CO_2 in N_2 at 40 °C for 5 min, followed by desorption by heating at 120 °C in the presence of N_2 or air for 5 min also. The result showed that the AFA exhibited a negligible change in CO_2 uptake implying that it was thermally stable throughout the cycling when N_2 was used as desorption purge gas. The result of the cyclic stability of the APTMS grafted silica in the presence of air as desorption purge gas also showed that the AFA experienced a minor loss (less than 1 %) in CO_2 uptake over 100 cycles. This finding was attributed to APTMS being the most stable amine species in the presence of air at elevated temperatures. The studies by Alkhabbaz et al. [82] along with those by Shen et al. [26], Qi et al., [87] and Ayub et al., [27], which involved cyclic stability testing over 50 to 100 cycles, suggest that thermal and cyclic failure in amine-functionalized adsorbents (AFAs) cannot be attributed solely to urea formation. This conclusion arises from observing instability at temperatures above 135 °C, the threshold temperature for urea formation. A summary of research works carried out on the thermal and cyclic stability of AFA is presented in Table 2 below.

The studies reviewed shed light on key mechanisms affecting the thermal and cyclic stability of AFA. Observations indicate that thermal degradation of AFA is a complex process influenced by mechanisms of amine and silica degradation, moisture sensitivity, type of support structure, chemisorbed species formation and amine type and functionalization method. These findings collectively suggest that the thermal and cyclic failure of AFA cannot be solely attributed to urea formation, as moisture has been seen to stabilise AFA beyond urea formation temperature, and therefore urges further research regarding the stabilization effect of water on AFA to comprehensively understand the underlying mechanisms and optimize AFA performance.

4. Factors affecting thermal and cyclic stability of silica-based amine functionalized adsorbents

A comprehensive analysis of existing research in the realm of thermal and cyclic stability indicates that numerous variables have been identified as influential in the context of silica-based AFA. These factors encompass a range of considerations, such as, the method employed for functionalization, the transformation of primary amines into secondary amines, the concept of double functionalization, the integration of mixed polyamines, amine volatility, amine molecular weight, the structural and textural characteristics of the supporting material and presence of impurities such as H_2S, SOx and NOx. The subsequent section provides a detailed examination of these factors.

4.1. Functionalization method

Method of functionalization is another factor that influences the thermal and cyclic stability of AFA. In the studies carried out by Refs. [27,48,61,68,77,78,116–120] it was noted that grafting produces more thermally stable AFA with better cyclic stability than impregnation. During grafting, the amine is covalently attached to the organosilane molecule, making it resist cyclic leaching more than what is obtained in the impregnation method. Yoon et al. [48] grafted TEPA onto MIL-(101)-Cr and noted that it withstood leaching more than its impregnated counterpart. During aminosilane grafting on silica, water molecules play a key role in hydrolyzing the silane groups, which enables the formation of stable siloxane (Si–O–Si) bonds between the aminosilane and the silica surface. This hydrolysis and subsequent condensation create a robust grafting structure, ensuring a strong attachment of the amine groups essential for effective CO_2 adsorption. Temperature is crucial in this process, as it influences the rate of hydrolysis and condensation reactions. For instance, Anyanwu et al. [121] examined the influence of water and grafting temperature on amine loading, CO_2 adsorption capacity, and cyclic stability using solution grafting method. The findings reveal that amine grafting at a low temperature of 30 °C, especially in the presence of water, results in higher amine loadings and enhanced CO_2 adsorption performance due to the increased pore space available for water before pore clogging occurs. Comparatively, dry grafting at 30 °C and 85 °C yielded similar amine loadings, indicating that temperature had limited effects on amine loading under dry conditions. Notably, wet grafting at 30 °C led to significantly higher amine loadings compared to wet grafting at 85 °C. This difference was attributed to the increased pore space available for water at 30 °C, consequently enhancing amine loading. Fig. 11 shows that adsorbents grafted at 30 °C exhibited improved cyclic stability under flue gas conditions, retaining their capacity after 10 adsorption-desorption cycles. The study also investigated the feasibility of applying low-temperature amine grafting to other silanes and mesoporous silica materials, demonstrating that these effects remained

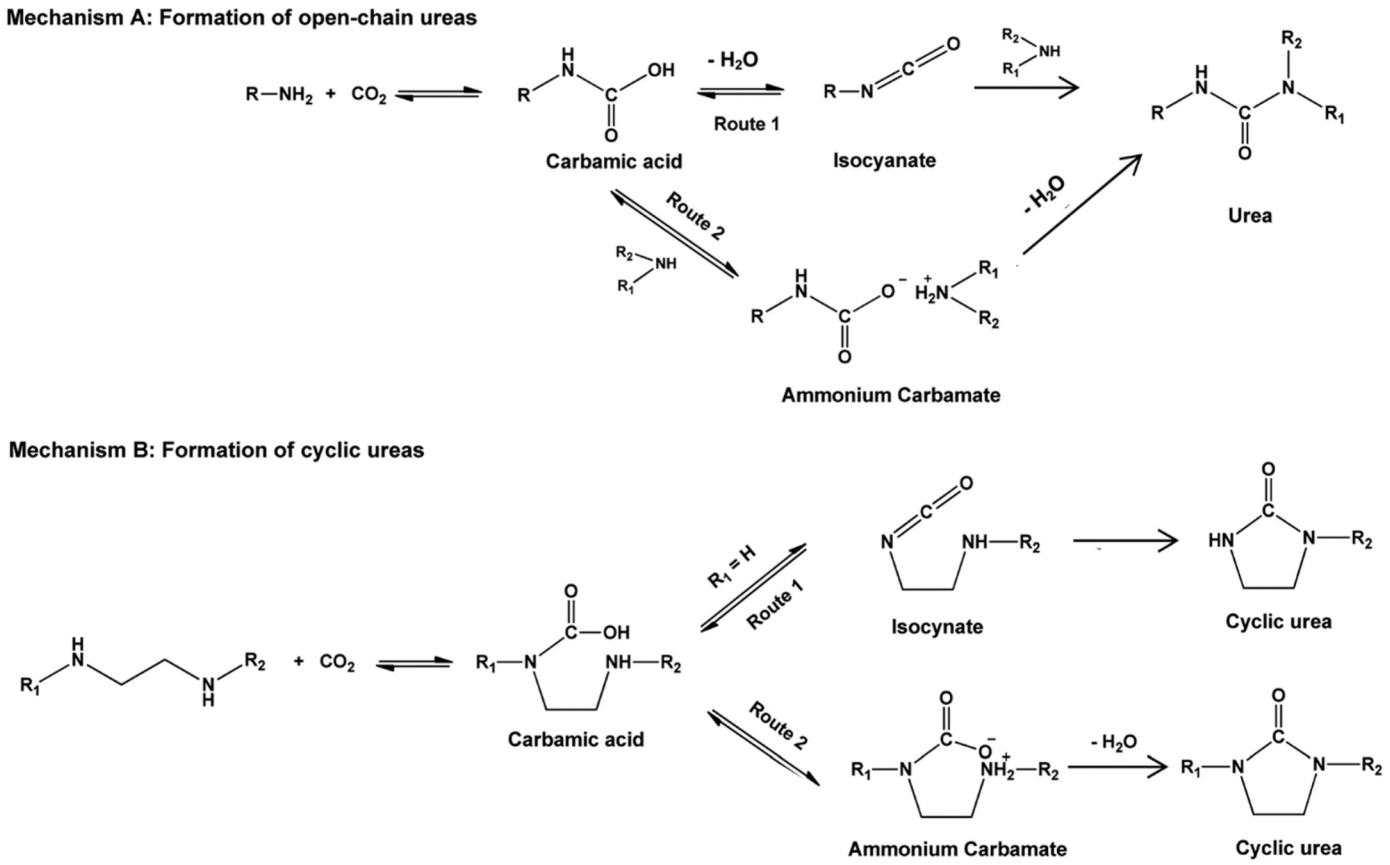

Fig. 10. Urea linkage formation in amine functionalised adsorbents [97].

consistent beyond the use of (3-Aminopropyl)trimethoxysilane and SBA-15.

The effect of moisture on stabilizing and enhancing amine loading during grafting was explained in a study conducted by Harlick et al. [122]. Their work suggested that adding water to the support material can increase the surface density of hydroxyl groups or initiate hydrolysis of unreacted alkoxy groups, thereby enhancing the surface coverage of amine-bearing species.

Under this procedure, as seen in Fig. 12, aminosilanes are linked through Si–O–Si bridges to other grafted aminosilanes thereby improving the thermal stability of the sorbent. Fig. 13 shows that in the case of dry-grafted TRI-PE-MCM-41, the release of methoxy accounted for 5−6 wt% of the total initial material mass. However, for wet-grafted TRI-MCM-41, the weight loss was notably lower, approximately 2–3 wt %.

For silica-based amine sorbents, presence of moisture in the gas stream has also been noted to improve the cyclic stability of the material as it deters the formation of urea and can also reverse completely CO_2 adsorption products of urea group by hydrolysis while maintaining a good sorbent stability and structural integrity [123]. In summary, these studies suggest that whether in grafting procedure or in the gas stream, presence of moisture fosters sorbent stability for silica-based sorbents.

Kolle et al., [67] established that, in addition to the conventional solution grafting approach, gas-phase grafting of diverse silanes onto mesoporous silica materials can be effectively conducted using the tumbling chemical vapor deposition (T-CVD) technique. Importantly, this gas-phase grafting process does not compromise the thermal stability of the resultant adsorbent as seen in Fig. 14. In a typical T-CVD process they employed, the support material underwent pre-treatment within a fixed-bed reactor at elevated temperatures. Subsequently, it was exposed to silane vapor in the presence of an inert gas or under vacuum conditions. This process effectively removed physiosorbed molecules using an inert gas flow. Notably, the gas-phase methodology achieved remarkable success in achieving significantly higher propylamine contents on the silica supports. This achievement indicates improved access to surface hydroxyl groups and enhanced packing of propylamine chains when compared to the conventional approach of solution grafting. Furthermore, gas-phase grafting offers advantages including increased grafting efficiency and reduced silane waste, which can be recycled. The CO_2 adsorbents produced via gas-phase grafting have exhibited superior CO_2 uptake and amine efficiency (CO_2/N) in comparison to those prepared through solution grafting methods.

Another method of functionalization which has not been widely utilized is the particle molecular layer deposition (MLD). MLD is a technique for precisely depositing thin layers of large organic molecules onto solid surfaces through self-limiting gas-phase reactions. This method allows for meticulous control over film thickness and cost-effective functionalization. In their research, Lai et al. [124] deposited APTES and TMPTA onto fumed silica substrates at 150 °C using MLD. As the number of MLD cycles increased, the sorbents displayed enhanced CO_2 adsorption capacities. The 10-cycle APTES and TMPTA sorbents exhibited adsorption capacities of 0.379 and 0.382 mmol CO_2/g, respectively. Notably, the 15-cycle APTES and TMPTA sorbents demonstrated even higher capacities at 0.64 and 1.86 mmol CO_2/g. This observed capacity increase with cycle numbers suggests the potential for further optimization. Furthermore, Lai et al. [124] assessed the thermal regeneration stability of the 10-cycle APTES and TMPTA sorbents over 25 cycles at a desorption temperature of 80 °C, revealing their relative stability throughout the process.

A novel method known as dry gel tumbling (DGT) was introduced by Kolle et al. [125] as a means of functionalizing porous supports with silanes, aimed at overcoming limitations associated with existing techniques such as the time-consuming nature of wet grafting, the high energy requirements of CVD, and the challenges posed by tumbling-CVD

Table 2
Summary of cyclic stability test of some amine functionalized adsorbents.

Sorbent type	Amine type	Loading	Adsorption condition	Desorption condition	Cyclic stability	Ref.
PE-MCM-41	PEI	40 wt%	400 ppm CO_2/N_2 at 25 °C	90 °C in N_2	20 cycles	[94]
MCM – 41	PEI and TEPA	40 wt%	10 % CO_2/N_2 at 35 °C	100 °C in N_2	10 cycles	[88]
MCM – 41	APTMS and TEPA	30 wt% and 40 wt% respectively	15 % CO_2/N_2 at 70 °C	100 °C in N_2	10 cycles	[89]
MCM – 41	AMP and TEPA	30 wt% and 30 wt% respectively	15 % CO_2/N_2 at 70 °C	100 °C in N_2	15 cycles	[90]
MCM – 41	TEPA	50 wt%	Pure CO_2, 5 % CO_2/N_2 at 75 °C	100 °C in N_2	6 cycles	[91]
MCM – 41	NH_2	50 wt%	40 mL/min N2, 10 mL/min CO_2 at 80 C	40 mL/min N_2 at 120 °C	5 cycles	[68]
MCM – 41	MEA and DEA	25 wt% each	CO_2 and N_2 at 1.5 bar	N_2 at 1 bar.	10 cycles	[98]
MCM-41	TEPA	70 wt%	12 % CO_2/N_2 at 75 °C	100 °C in N_2	5 cycles	[99]
SBA – 15	PEI	50 wt%	Pure CO_2, at 45 °C	110 °C in vacuum	4 cycles	[100]
SBA – 15	TEPA and DEA	30 wt% and 20 wt% respectively	Water saturated CO_2 and 5 % CO_2/N_2 at 75 °C	100 °C in Ar	6 cycles	[101]
SBA – 15	AN-modified TEPA and TEPA	50 wt%	Pure CO_2, at 25 °C	100 °C in N_2	12 cycles	[102]
SBA – 15	TEPA	50 wt%	Pure CO_2, 5 % CO_2/N_2 at 75 °C	100 °C in He	7 cycles	[103]
SBA – 15	PPG	50 wt%	10 % CO_2/N_2 at 30 °C	120 °C in He	5 cycles	[104]
Silica MCF	PEI	50 wt%	15 % CO_2/N_2 at 75 °C	75 °C in Ar	8 cycles	[92]
Silica MCF	TEPA	70 wt%	10 % CO_2/N_2 at 75 °C	100 °C in He	8 cycles	[93]
Silica MCF	PEI and PAA	8.96 and 7.24 mmol/g respectively	10 % CO_2/N_2 at 25 °C	110 °C in Ar	3 cycles	[105]
Silica MCF	PAA	6.13 mmol/g	10 % CO_2/N_2 at 30 °C	120 °C in He	5 cycles	[82]
Nano-Silica	PEHA	4.24 mmol/g	Pure CO_2 at 90 °C	120 °C in Air	50 cycles	[106]
Silica MCF	GPAA	5.71 mmol/g	10 % CO_2/N_2 at 30 °C	120 °C in He	5 cycles	[82]
MSU-F	TEPA and DEA	40 and 30 wt% respectively	Pure CO_2 at 40 °C	50 C in air	5 cycles	[107]
MSU – 1	TEPA	50 wt%	10 % CO_2/N_2 at 75 °C	100 °C in N_2	12 cycles	[108]
MSU – J	TEPA	15.58 wt%	Pure CO_2 at 25 °C	100 °C in vacuum	6 cycles	[109]
3D-printed silica monolith	PEI and TEPA	13.2 and 11.5 mmol/g	10 % CO_2/N_2 at 25 °C	110 °C in N_2	5 cycles	[57]
Homemade MS-silica	AM-modified TEPA	50 wt%	Pure CO_2 at 25 °C	100 °C in Air	12 cycles	[110]
Homemade MS-silica	TEPA	50 wt%	Pure CO_2 at 25 °C	100 °C in Air	5 cycles	[110]
Hierarchical silica monolith	PEI and TEPA	65 wt%	Pure CO_2 at 75 °C	75 °C in N_2	5 cycles	[111]
Silica microspheres	Epoxide-functionalized TEPA		15 % CO_2/N_2 at 30 °C	90 °C in N_2	10 cycles	[112]
	O/N ratio 0.42	7.3 mmol/g				
	O/N ratio 0.64	8.6 mmol/g				
	O/N ratio 0.82	10.1 mmol/g				
Silica nanotubes	TEPA	50 wt%	10 % CO_2/N_2 at 75 °C	100 °C in N_2	5 cycles	[113]
Silica nanospheres	TEPA	50 wt%	Pure CO_2 at 75 °C	100 °C in vacuum	9 cycles	[114]
Silica nanoparticle	APTES	50 wt%	Pure CO_2 at 25 °C	100 °C in Air	5 cycles	[115]
G-10 Silica	APTMS	1.14 mmol/g	30 % CO_2/N_2 at 40 °C	120 °C in N_2	100 cycles	[27]

with silanes. This innovative approach integrates aspects of both solution and gas phase grafting procedures. As seen in Fig. 15, initially, organosilane and support are mixed in a volatile solvent, followed by solvent recovery to yield a dry gel. Subsequently, the powder undergoes tumbling at approximately 110 °C for several hours, followed by thermal treatment at 80 °C. DGT was utilized to fabricate amine-grafted CO_2 adsorbents (AGAs) and compared with materials from water-aided solution grafting.

DGT emerged as a practical method for grafting various organosilanes characterized by low oxidation stability, high boiling points, and low vapor pressures, which may pose challenges for gas phase grafting. Kolle et al. suggest that DGT, employing easily recoverable volatile solvent and low synthesis temperature, offers a sustainable, reliable, and cost-effective approach for large-scale AGA production. Materials synthesized via DGT surpassed those from water-aided grafting, demonstrating notably high amine content (4.53 mmol/g), CO_2 capacity (2.08 mmol/g), amine efficiency (0.46) and were likewise cyclically and thermally stable as shown in Fig. 16. The exceptional performance of DGT can be attributed to its maximal incorporation of organosilanes during grafting, ensuring efficient and high-yield reactions between surface silanol groups and alkoxyl groups of the silane, with grafting efficiencies exceeding 95 % for propylamine-grafted adsorbents.

4.2. Conversion of primary amines to secondary amines

The degree of conversion of primary amines to secondary amines in the functionalization process can exert a notable influence on stability. In many cases, secondary amines demonstrate enhanced stability in comparison to primary amines, owing to the stabilizing influence of the alkyl or aryl groups in them. Zhang et al. [110] in a bid to improve on the desorption qualities of TEPA functionalized SBA-15 adsorbent modified TEPA with acrylamide, and then impregnated it to SBA-15. This modification resulted in the conversion of TEPA into a secondary amine due to the Michael addition reaction. The resulting material exhibited a higher adsorption capacity of 159.1 mg/g-adsorbent at 25 °C and an improved cyclic stability of 12 cycles as against 5 cycles of the non-functionalized amine, thus indicating that conversion of primary amines can aid improve the thermal and cyclic stability of AFA. In another research by Parl et al., [112] facile functionalization with 1, 2-epoxybutane (EB) was carried out on TEPA to investigate the

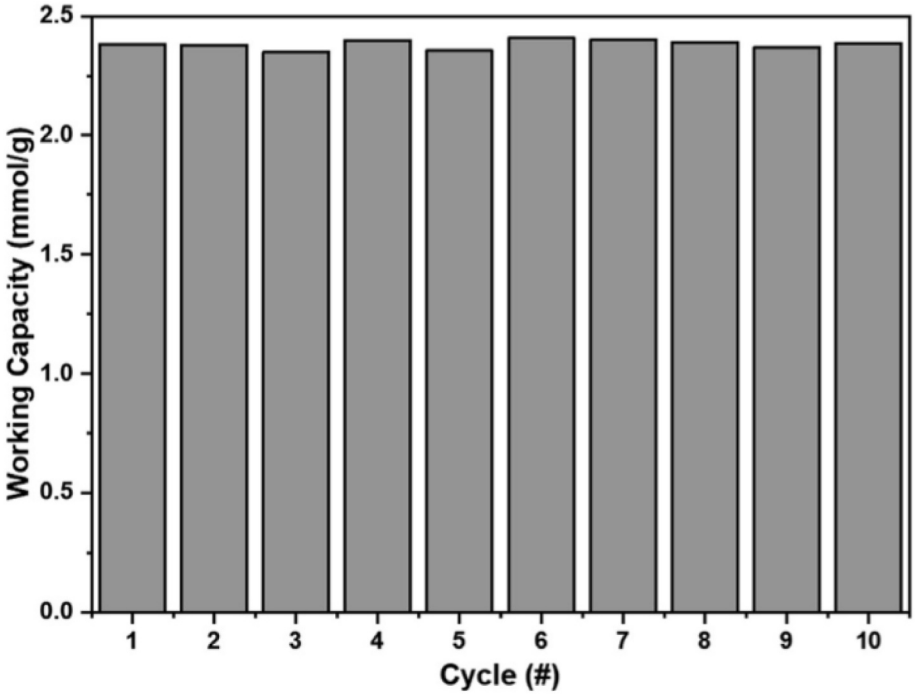

Fig. 11. Cyclic stability of wet grafted APTES SBA-15 adsorbent at 30 °C [121].

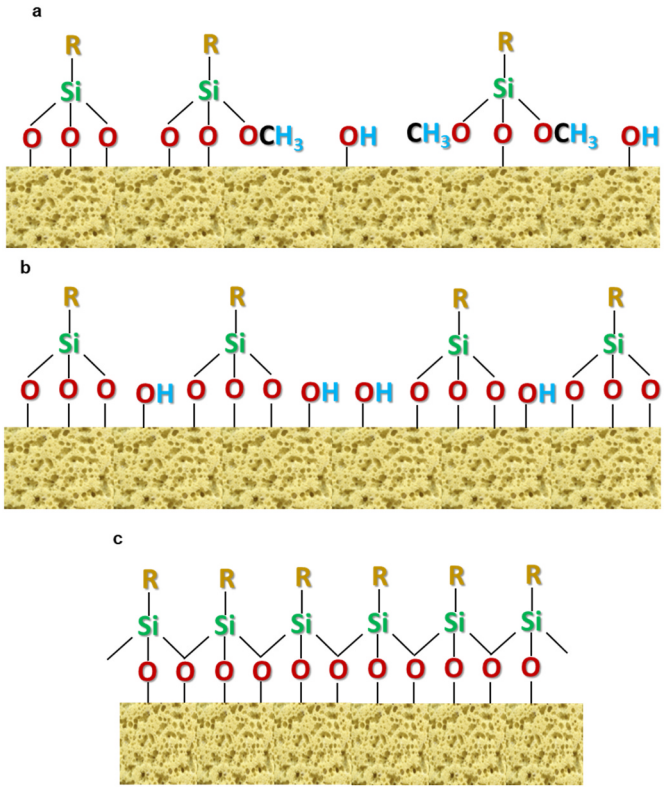

Fig. 12. Proposed surface modification of silica-based sorbents due to (a) dry grafting of aminosilane (b) increase in surface density of hydroxyl groups and hydrolysis of unreacted alkoxy groups during wet grafting and (c) formation of Si–*O*–Si bridges. Adapted from [122].

resulting material effect on thermal stability. This modification was done in an EB/TEPA ratio of 2:1, 3:1, and 4:1 corresponding to molar O/N ratios of 0.42, 0.64, and 0.82 respectively as seen in Fig. 17a. It was

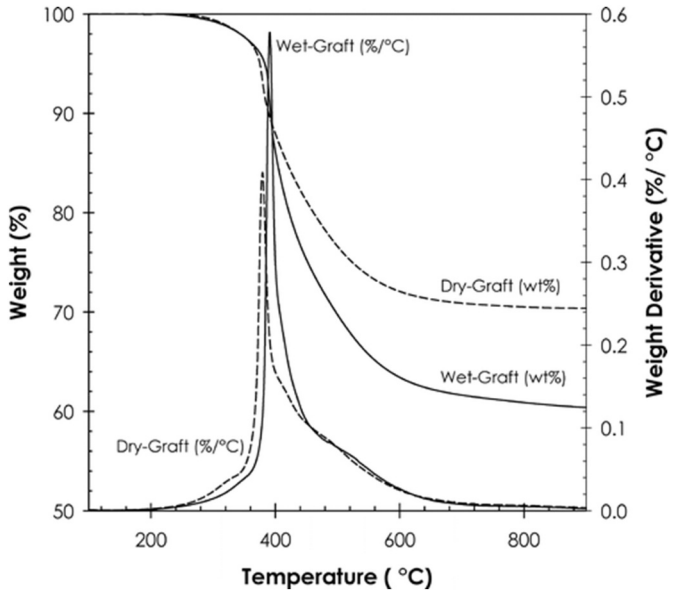

Fig. 13. Effect of moisture addition on grafting of aminosilanes on silica support [122].

observed that the modification of TEPA increased its molecular weight and subsequently the thermal stability, also the adsorption kinetics was improved because of the bulky 2-hydroxybutyl groups, which induced enhancement of intermolecular chain distance. Viscosity of the modified TEPA was also noticed to increase with increasing degree of EB-functionalization.

4.3. *Double functionalization*

Amine double functionalization of adsorbents has also shown to possess good prospects for improving the thermal and cyclic stability of AFA. Some studies investigate this approach, where multiple types of

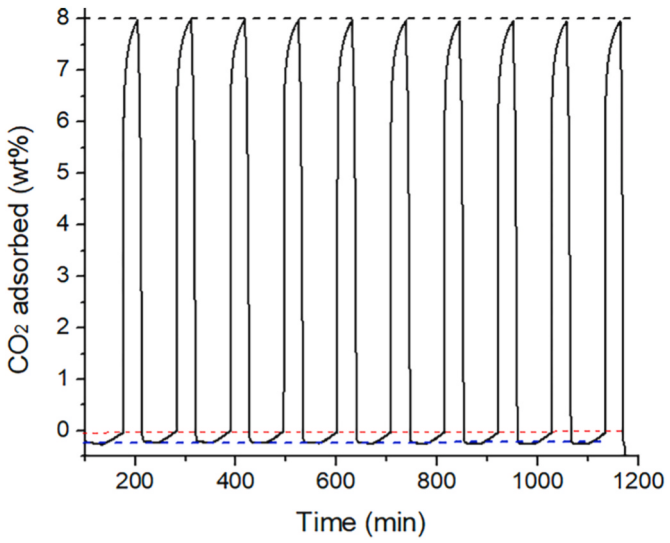

Fig. 14. Cyclic Adsorption and desorption of CO_2 in T-CVD derived material [67].

amines are incorporated into the sorbent. In a study carried out by Ref. [126] aimed at relieving amine agglomeration in solid amine adsorbent, a novel double-functionalized adsorbent was synthesized by first grafting 3-aminopropyltriethoxysilane (APTES) into mesoporous silica molecular sieves followed by impregnation of the mesoporous silica molecular sieves with TEPA by 0, 40, 50, 60 and 70 wt%. It was shown that an increase in the thermal stability of the AFA was achieved because of the effective hydrogen bonding which existed between the amine and the silanol groups on the sorbent surface. The grafted APTES through reaction with the silanol groups of the support surface forms a spatial separation structure that provides space for TEPA to disperse and be immobilized in the sorbent. Hence, with an increase in the TEPA loading, the thermal stability increases. The cyclic stability study showed that the adsorbent retains about 5.2 mmol of CO_2/g of adsorbent after 15 adsorption/desorption cycles. Fig. 18 shows thermal decomposition of the adsorbent initiates at 250 °C, demonstrating a noteworthy enhancement in comparison to an AFA functionalized solely with TEPA or APTES.

In another study by Refs. [73,115], double functionalization of silica nanoparticles was carried out by first functionalizing the silica nanoparticle with APTES, thereafter, double functionalization with PAMAM dendrons (G2), PAMAM-PEG dendrons (G3) and Lys-Lys peptide were carried out, respectively. Result of the thermal stability shows that weight loss for SiO_2@APTES, SiO_2@(G2), SiO_2@(G3) PEG and SiO_2@Lys-Lys samples was noticed at 200–350 °C because of a probable decomposition of dendritic branches and peptide cleavage. The SiO_2@Lys-Lys showed a third stage of weight loss 350–420 °C, with a maximum occurring at ~385 °C, likely due to the decomposition of the remaining amino acid branches. Overall, the double functionalization of the silica nanoparticle proved to have better thermal stability than functionalizing with APTES alone, which was also verified by Sanz et al. [25] in similar research. In another study, Fang et al. [127] determined the role of amine or hydroxyl functional groups additives on silica-based PEI adsorbents, SiO_2 aerogels were prepared using the sol-gel method and methyl alkylation reaction using TEOS as silicon sources. Thereafter, PEI was grafted into the sorbent to form polyethyleneimine (PEI/SiO_2) adsorbents for CO_2 adsorption and was dopped with hexamethyldisilyamine (HMDS), triethylamine (TEA), ethylene glycol (EG), polyethylene glycol (PEG), imidazole (IM), N- [3- (Trimethoxy silyl) propyl] ethylenediamine (N–Y) and 2-methylimidazole (2-MI) separately to obtain eight samples. The aim of the research was to determine the effect these additives on the thermal stability and adsorption capacity of the PEI/SiO_2 adsorbent. It was reported that the maximum CO_2 adsorption capacity (1.8 mmol/g) was obtained from the sample doped with N–Y, which was composed of 45 % PEI and 15 % N–Y. N–Y dopped PEI/SIO_2 adsorbent also possessed better thermal stability than SA-PEI-60 % in nitrogen when heated from room temperature to 800 °C at a heating rate of 10 °C/min. Vu et al. [128] showed that the

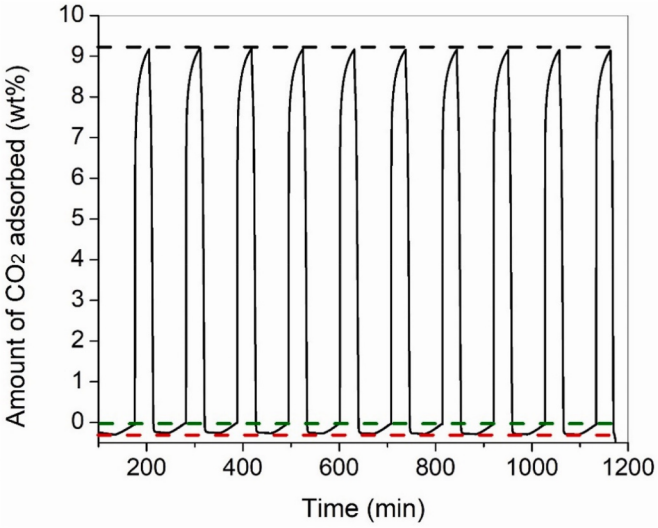

Fig. 16. Cyclic Adsorption and desorption of CO_2 in DGT derived material [125].

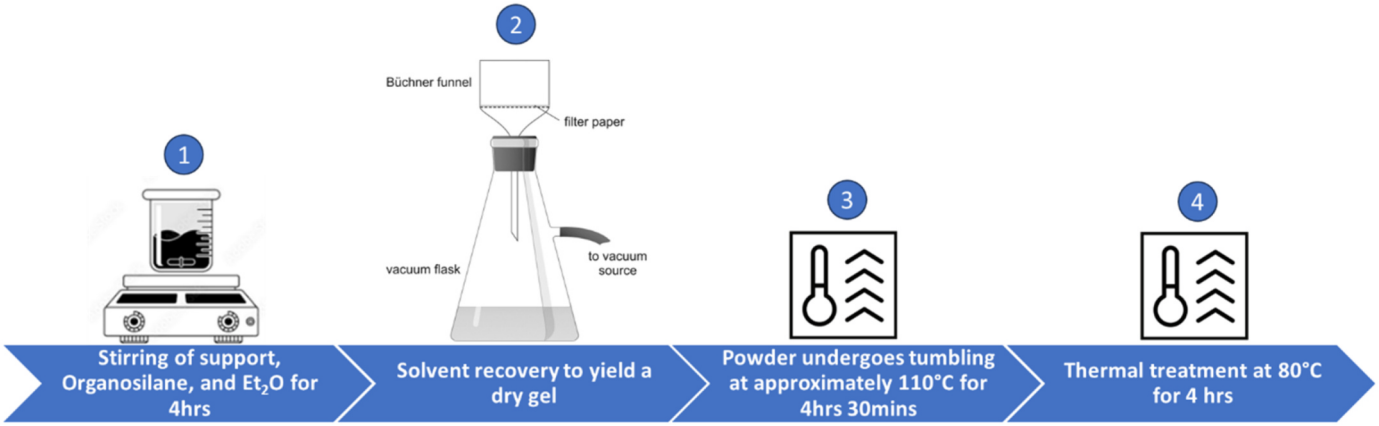

Fig. 15. Illustration of dry gel tumbling method for functionalizing amine sorbents.

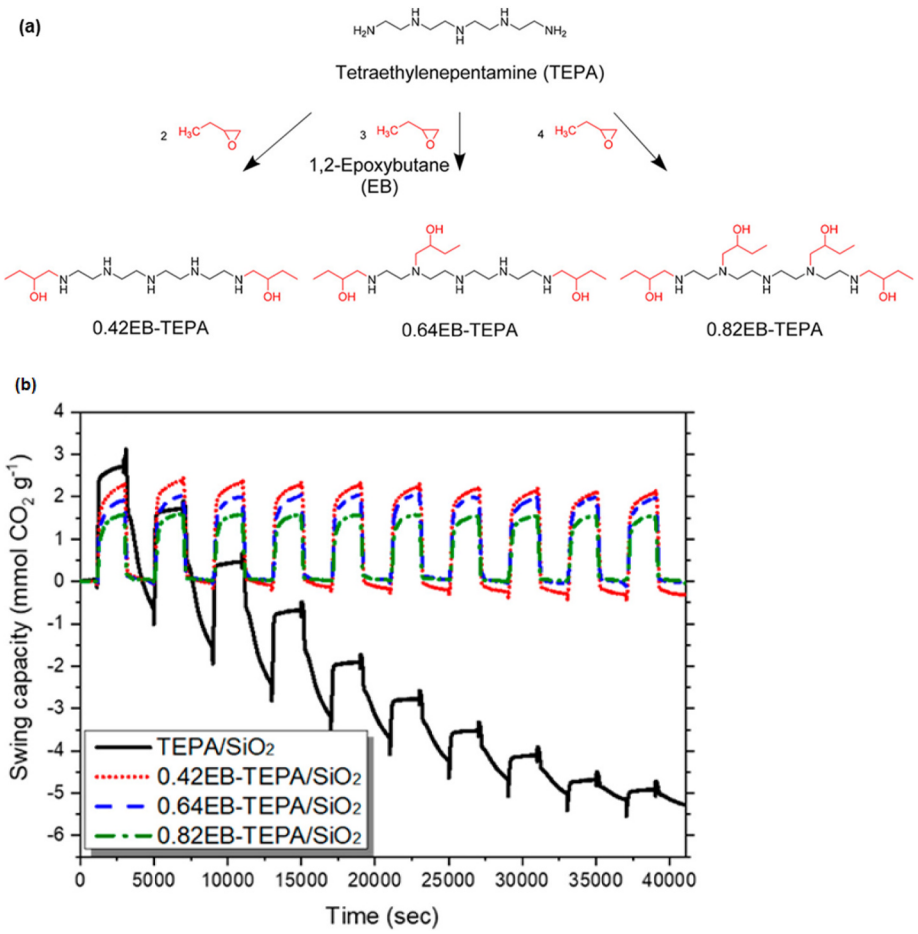

Fig. 17. (a) Schematic representation of EB-based chemical functionalization of TEPA with different EB/TEPA molar ratios. (b) CO_2 adsorption/desorption cycles of TEPA functionalized adsorbent and EB modified TEPA functionalized adsorbent [112].

incorporation of imidazoles (Ims) with electron-donating groups into tetraethylenepentamine (TEPA) resulted in significant enhancements in CO_2 adsorption capabilities, reduced energy consumption, and improved thermal stability of sorbents. These observed synergistic effects were attributed to the proton-accepting capacity of Ims and their facilitation of proton and CO_2 diffusion to subsurface reactive sites. Among the various tested sorbents, an optimized blend of 30 % 4MIm and 40 % TEPA impregnated into a mesostructured cellular silica foam exhibited superior CO_2 adsorption performance and thermal stability. This sorbent demonstrated a remarkable adsorption capacity of 4.88 mmol/g and a working capacity of 4.15 mmol/g at 40 °C and 100 kPa CO_2, along with a low heat of adsorption (69 kJ/mol) under conditions of 40 °C and atmospheric pressure as seen in Fig. 19. Furthermore, it achieved a maximum CO_2 uptake of 5.88 mmol/g under conditions of 50 °C and 100 kPa CO_2.

A combination of double functionalization and support modification as a means of improving the thermal and cyclic stability of AFA was investigated by Lin et al., [129] Zeolite and Silica materials were used to form a micro-/mesoporous three-dimensional cross-straight structural composite which was double functionalized by first grafting N1-(3-trimethoxysilyl-propyl)diethylenetriamine (TMPTA) onto the composite sorbent support, and then impregnating with 50 wt% PEI and 60 wt% TEPA separately to form two samples. The composite sorbent support possessed better textural properties and both samples showed improvement in thermal and cyclic stability by having a capture capacity of 6.28 $mmolg^{-1}$ and 4.69 $mmolg^{-1}$ for AZK-T60 and AZK-P50 respectively, after five cycles operating at an adsorption and desorption temperature of 75 °C and 110 °C respectively. When compared with their amine functionalized unmodified sorbent counterpart, this is seen as an improvement. In similar research carried out by Ge et al., [130] a composite support sorbent ZSM-5/SBA-16 was formed by using non-ionic tri-block copolymer Pluronic (F127) as a template, tetraethyl orthosilicate (TEOS) as a silicon source and ZSM-5 zeolite as part of silicon aluminium source by an embedding method. ZSM-5/SBA-16 was bifunctionalised with 55 wt% of grafted APTES and impregnated TEPA. As seen in the earlier research conducted by Lin et al., [129] the double functionalized ZSM-5/SBA-16 possessed higher nitrogen content and demonstrated better properties such as pore volume, pore size, and surface area. it was observed that the adsorption process due to the composite support sorbent comprised a synergy between physical and chemical adsorption. The adsorption capacity of ZS-A-T-55 exhibited just 8.2 % weight loss after five adsorption/desorption recycles. Jia et al. [131] also reported similar results after carrying out the same research.

4.4. *Mixed polyamines*

Using a mixture of different polyamines for functionalization can be a strategy to enhance stability as seen in a study carried out by He et al. [132] to reduce the high desorption temperature of current DAC adsorbents. 50 wt% DEA and TEPA was impregnated into the mesoporous SBA-15 which enhanced the CO_2 adsorption and desorption kinetics due to the hydroxyl groups from DEA. Various samples of the adsorbent were obtained by changing the weight ratio of TEPA to DEA as follows 1/4, 1/2, 1/1, 2/1, 4/1. Results of the thermal and cyclic stability indicated that the mixed polyamine functionalized adsorbent performs better than the DEA functionalized adsorbent, loosens agglomeration of TEPA

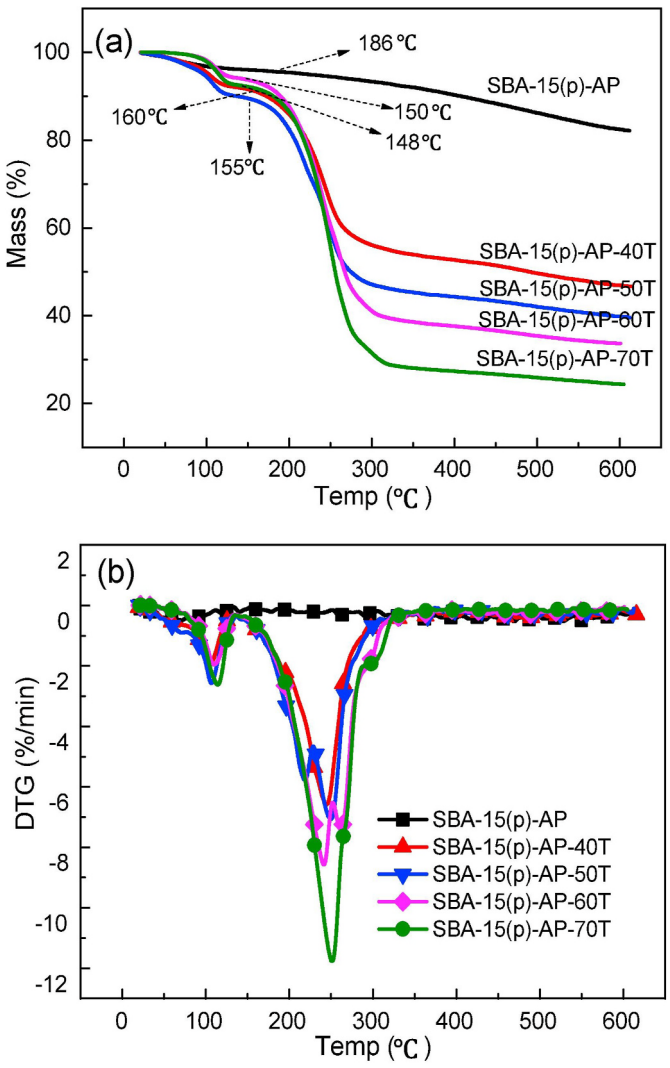

Fig. 18. (a) Thermal stability profiles of SBA–15(p)–AP–XT. (b) DTG profiles of SBA–15(p)–AP–XT [126].

which enhances faster diffusion of the CO_2 molecules, increases mass transfer and capture capacity also, the cyclic stability was also improved to 10 cycles. In a similar study, Dao et al. [133] examined the material characteristics of MSU-F and its amine-impregnated variants. It was noted that the blend of DEA and TEPA exhibited notable improvements in the regeneration characteristics of the sorbents. MSU-F, when loaded with a combination of 40 wt % TEPA and 30 wt % DEA, demonstrated exceptional adsorption capacity (5.91 mmol/g at 50 °C and 100 kPa), a substantial heat of adsorption (80 kJ/mol), robust cyclic stability, and strong selectivity for CO_2/N_2 separation. The experimental findings from the study validate that the addition of DEA enhances the diffusivity of CO_2 in impregnated amines. This improvement can be attributed to the dense clustering of TEPA carbamate and protonated TEPA, which is loosened by the presence of other amines with moderate reactivity, such as DEA, causing more adsorption sites to be created as seen in Fig. 20. The enhanced CO_2 diffusion is expected to facilitate both desorption and adsorption processes.

Liu et al. [134] impregnated a Silica Mesocellular foam with a blend of 70 wt% PEI and TEPA to achieve higher CO_2 capacities, faster adsorption kinetics and improved adsorbent stability. It observed that PEI-TEPA binary amine sorbent possessed higher thermal stability and cyclic performance than the supported PEI or TEPA sorbent because the CO_2 capacity of the PEI-TEPA sorbent decreased slightly by 3.4 % from 3.24 to 3.13 mmol/g over the 50 cycles test. According to Liu et al. [134] result of the cyclic test probably suggests that the co-impregnated PEI-TEPA binary amine suppressed the irreversible urea formation during CO_2 adsorption and desorption cycles. In another study, Zhao et al. [135] co-impregnated a hierarchical bimodal mesoporous silica (HMS) synthesized by using P123 as template through a partitioned cooperative self-assembly process with 60 wt% TEPA and 10 wt% bis (2-aminopropyl ether) (PEA) to achieve a highly efficient nano-composite for CO_2 capture. The synthesized HMS possessed large pore volumes and surface areas which facilitated increased amine loading and dispersion within the sorbent matrix. Results of the study showed that the HMS - TEPA 60 wt% - PEA 10 wt% was thermally stable for 10 adsorption – desorption cycles and performed better than HMS – TEPA 70 wt% counterpart. This draws the conclusion that co-impregnating HMS with TEPA 60 wt% - PEA 10 wt% increased the thermal and cyclic stability of the AFA.

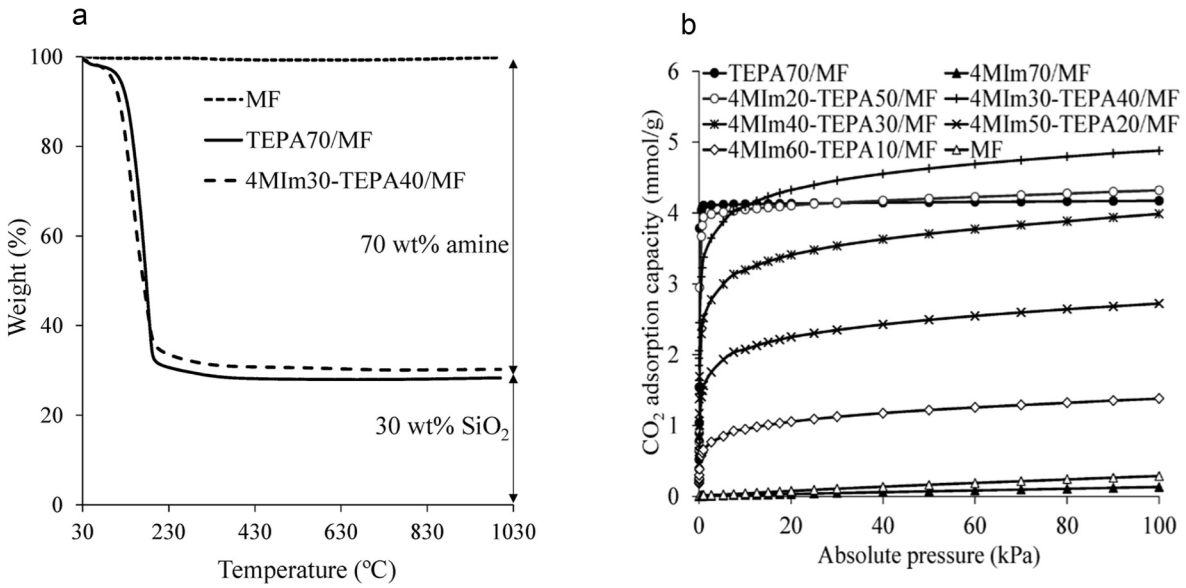

Fig. 19. (a) Displays the thermogravimetric profiles of pure MF and MF impregnated with 70 wt% amine (TEPA70 and 4MIm30-TEPA40). In (b), the CO_2 adsorption isotherms for 4MImx-TEPAy/MF adsorbents at 40 °C are presented [128].

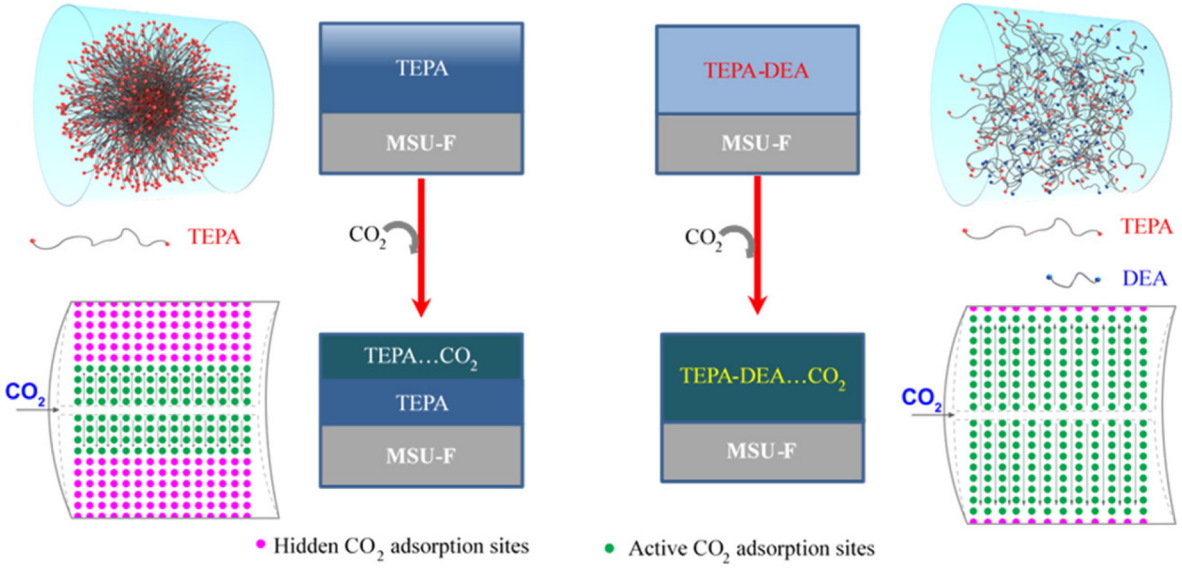

Fig. 20. Proposed mechanism for CO_2 adsorption in TEPA/MSU-F and TEPA/DEA/MSU-F [133].

4.5. Amine volatility

The volatility of the amine compounds used in AFAs can affect their stability. Highly volatile amines might be prone to evaporation or decomposition at elevated temperatures, reducing the long-term stability of the sorbent. Researchers such as [52,136–139] investigated the thermal and cyclic stability of PEI functionalized silica-based adsorbents. It was observed in all the studies cited that the thermal stability of an AFA could be influenced by the volatility of the amine used. Xu et al. [136] observed that increase in PEI loading from 30 wt% to 50 wt% increased the CO_2 capture capacity of the AFA, however, increase of PEI loading to 75 wt% resulted in maximum weight loss at higher temperature. This observation was attributed to the decrease in the synergetic effect existing between the PEI and the sorbent pores because of the coating of the outer surface of the molecular sieve crystal. This excess coating makes the crystal to behave as a bulk PEI which is volatile at high temperatures. Wang et al. [138] observed that higher loadings of PEI cause agglomeration on the external surface of the sorbent hindering access to adsorption site, and eventually causing the AFA to behave as a bulk PEI. An optimum loading of 50 wt% was therefore suggested since adsorption is highest at this loading percentage due to better synergy between the pores and PEI. Loadings beyond this value at temperatures above 75 °C favour volatility of PEI, weight loss in amine and extensive degradation in the presence of dry CO_2 [139]. In a study by Yamada et al. [140], a series of five TEPA derivatives was synthesized. These derivatives involved the introduction of three alkyl and two hydroxyalkyl substituents into the amino groups of TEPA. Subsequently, TEPA and its derivatives were employed for impregnating MSU-F. Notably, the hydroxyalkyl tetraethylenepentamines, particularly EtOH-TEPA/MSU-F and PrOH-TEPA/MSU-F, exhibited marginally higher surface areas and pore volumes when compared to TEPA/MSU-F and alkyl TEPA/MSU-F. A comprehensive thermogravimetric analysis as seen in Fig. 21 highlighted the reduced volatility of hydroxyalkyl TEPAs in comparison to TEPA and alkyl TEPAs. This decrease in volatility contributed to improved thermal stability and was attributed to robust molecular interactions and potential polymerization phenomena. It is noteworthy that a significant portion of the hydroxyalkyl TEPA resisted volatilization, even at elevated temperatures exceeding 400 °C, remaining affixed to the sorbent. This behaviour might be ascribed to the possible polymerization of hydroxyalkyl TEPA, as alcohols can undergo transformation into ethers when subjected to heat. Furthermore, viscosity measurements revealed a notably high viscosity for PrOH-TEPA, which

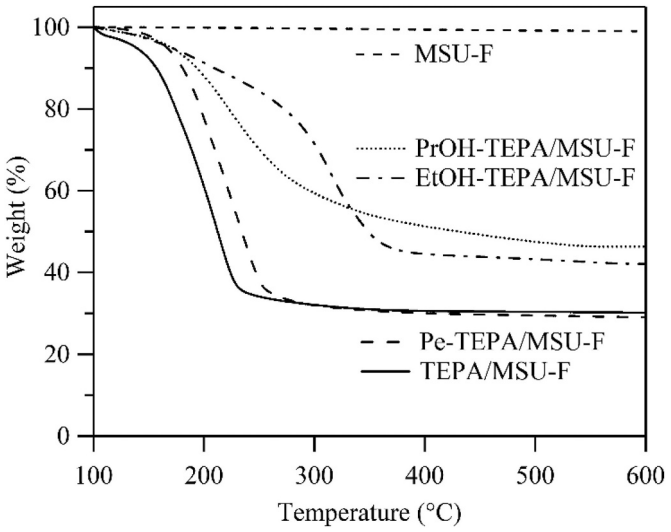

Fig. 21. Thermogravimetric (TG) curves for both MSU-F and the solid sorbents impregnated with amines [140].

can be explained by the presence of dense hydrogen bonding networks.

4.6. Amine molecular weight

The molecular weight of the amines employed plays a crucial role. Generally, higher molecular weight amines tend to provide better stability [141], as they have larger and more complex structures that can withstand thermal stress. Zhi-lin et al., [88] carried out a study on the CO_2 adsorption properties and thermal stability of different amine-impregnated MCM-41 materials. 40 wt% each of EDA, TEPA and PEI with molecular weights of 600 (PEI600) and 800 (PEI1800) were used to functionalise MCM-41 crystals via impregnation. it was observed that amines with higher molecular weights are more thermally stable than amines with lower molecular weights as the thermal stability was in this order EDA-MCM-41 <TEPA-MCM-41<PEI600-MCM-41<PEI1800-MCM-41. When the samples were regenerated at 100 °C under a pure nitrogen atmosphere, EDA was observed to be very thermally unstable as it volatilizes easily, the CO_2 adsorption capacity of TEPA decreased by 7.4 % after ten recycles in contrast to less than 1 % for both PEI600-MCM-41 and PEI1800-MCM-41.

This study carried out by Zhi-lin et al., [88] linked the thermal instabilities of EDA and TEPA functionalized MCM-41 to being short chain molecules with lower molecular weights making it difficult to be impregnated on the carrier surface. An alternative rationale for this occurrence is elucidated in the research conducted by Moon et al. [142] In their study, they postulated that the improved thermal stability observed in polyethyleneimine (PEI) compared to tetraethylenepentamine (TEPA) is attributable to the formation of distinct associations, specifically monodentate or bidentate interactions in TEPA and multidentate interactions in PEI, with the silica surfaces. This is primarily attributed to differences in molecular chain length and weight. The multidentate associations in PEI facilitate a greater degree of interaction between the amine moieties and the silica surface, resulting in enhanced thermal stability when compared to the TEPA counterpart. From the graphs in Fig. 22, it is seen that amines with higher molecular weights are more thermally stable than amines with lower molecular weights.

Heydari-Gorji et al. [139] had similar observation while investigating the thermal, oxidative and CO_2 – induced degradation of PEI supported adsorbents. PEI with molecular weights of 400, 600, and 2500 were impregnated into SBA-15 crystals and at 75 °C, weight losses of 2.6, 0.3 and 0 % were recorded respectively for the various molecular weights being investigated. At a higher temperature of 120 °C, weight losses of 22.5, 4.0, and 1.3 % were recorded respectively, and at 150 °C, PEI with molecular weights of 2500 showed thermal stability with weight loss of only 5 %. Heydari-Gorji et al. [139]work also showed that regeneration temperature would adversely affect thermal stability.

4.7. Support morphology and textural properties

Another factor identified as a contributor to thermal stability of AFA is the support textural properties. The physical characteristics of the support material, such as its morphology and textural properties (e.g., surface area, pore size, and pore volume), can significantly influence stability. These properties affect the accessibility and dispersion of amines within the support.

In the work carried out by Sakwa-Novak et al., [143] it was reported that a fundamental understanding of how the properties of oxide support, such as pore structure, particle morphology, and surface properties affect the efficiency of the guest polymer in its interactions with CO_2 is utmost in the design and optimization of the AFA materials. To this end, their study included a prepared array of SBA-15 support materials having different textural and morphological properties, as well as different content of zirconium doped into SBA-15. Zirconium was incorporated into the SBA-15 either during the synthesis of the SBA-15 or post synthetically via deposition of Zr species onto pure-silica SBA-15. The dopped Zr SBA-15 altered the surface area, pore volume, pore size, reduced micro-porosity, and provided a large, well-defined particle when compared to the parent SBA-15. These alterations improved the CO_2 capture capacity of SBA-15 impregnated with PEI by a maximum of ~60 % due to the significant microporosity possessed by the Zr dopped SBA-15.

Kuwahara et al. [144] also highlighted that the CO_2 adsorption characteristics, cyclic and thermal stabilities of a PEI functionalized silica sorbent can be improved upon by altering the acid/base properties of the oxide support through doping the silica support with Zr. The introduction of an optimal amount of Zr (Zr/Si ~ 0.07) resulted in a significant improvement in the CO_2 capacity, cyclic and thermal stability, and amine efficiency under dilute (simulated flue gas) and ultra-dilute (simulated ambient air) conditions. DTG analysis of the Zr doped AFA showed that maximum weight loss occurred at a temperature of 211 °C instead of 181 °C for the Zr free AFA.

In addition to this, the adsorption–desorption test showed that Zr dopped AFA showed better cyclic performance than the Zr free counterpart. Modification of the sorbent support has also been carried out by Kuwahara et al. [145] using other elements such as Aluminium (Al), Titanium (Ti), and Cerium (Ce) and then compared with Zr dopped PEI/SBA – 15 [141]. They focused on the impact of heteroatom type and loading on sorbent structure and adsorption performance. Outcome of the study shows that at optimal metal concentrations, the CO_2 capture capacity with 400 ppm CO_2 gases increases in the order of: PEI/S-BA-15<PEI/Al-SBA-15<PEI/Ti-SBA-15<PEI/Ce-SBA-15<PEI/Zr-SB-A-15. To determine the thermal and cyclic stability of the adsorbents, several selected composite adsorbents containing the various heteroatoms were subjected to multiple CO_2 adsorption/desorption cycles at a temperature of 25 °C for the adsorption phase, while for the desorption phase, CO_2 was desorbed from the surface in pure Ar atmosphere at 110 °C for 3 h. The result of the thermal and cyclic stability test reveals that conventional PEI/SBA–15 declines steadily in capture capacity due to amine weight loss or urea formation at increased temperature. The conventional PEI/SBA–15 lost 34 % of its adsorption capacity after four cycles, conversely, PEI/$Ti_{4.3}$-SBA-15 and PEI/Zr_7.0-SBA-15 showed better thermal and cyclic stability by losing only 5 % and 2 % of its ability to reversibly reabsorb CO_2 under dry conditions after 4 cycles.

In a related investigation, conducted by Jahandar et al. [146], the influence of aluminium integration into the structure of MCM-41 silica on its CO_2 adsorption characteristics and resistance to hydrothermal degradation during CO_2 capture, particularly in the context of steam-based regeneration, was examined. Fig. 23 schematically illustrates the material synthesis procedurre and the study outcome. The findings reveal that the inclusion of aluminium within the MCM-41 silica framework enhances the hydrothermal stability of amine-modified adsorbents during steam regeneration processes.

This improvement is attributed to aluminium's capacity to establish stable Al–*O*–Si linkages, which exhibit greater resistance to hydrolysis

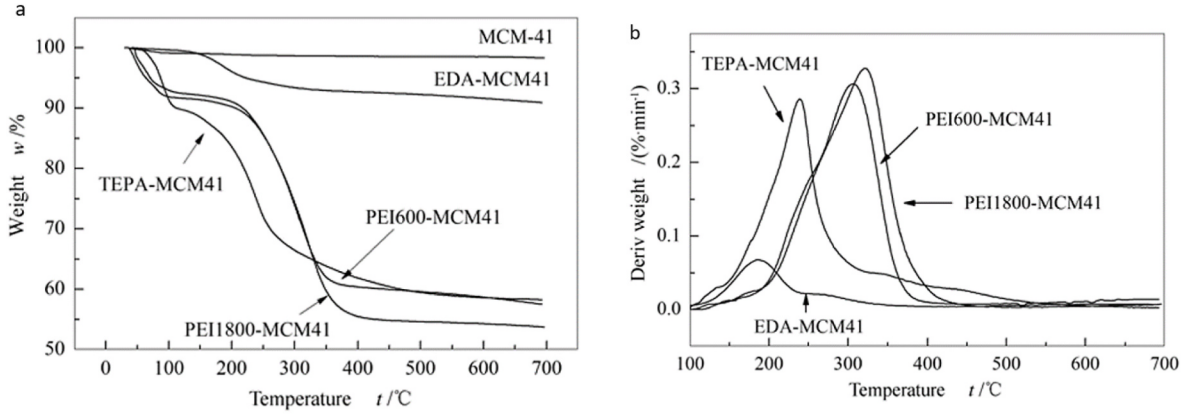

Fig. 22. (a) TG plot of the various AFA showing weight loss at different temperatures and (b) DTG plot of the various AFA showing weight change rate at different temperatures [88].

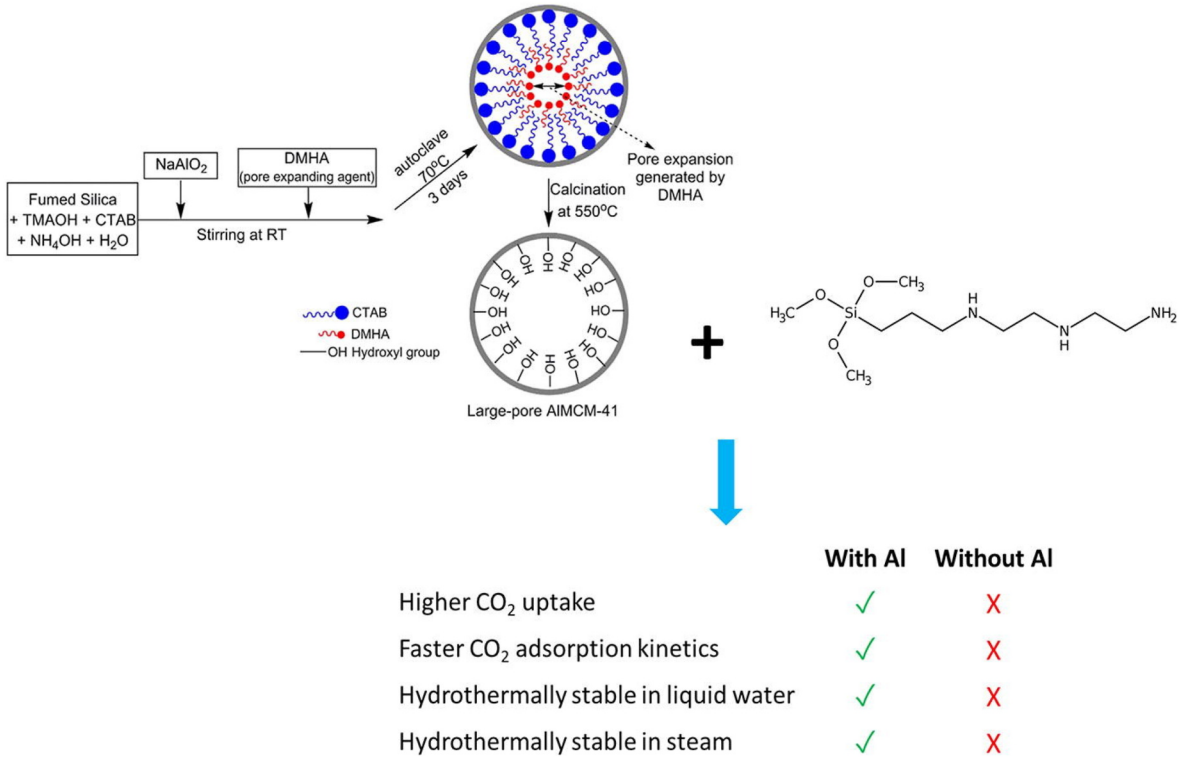

Fig. 23. Schematics of the material synthesis procedure and the study outcome [146].

compared to the Si–*O*–Si bonds. The amine-functionalized MCM-41 aluminosilicate materials demonstrated superior CO_2 uptake and faster adsorption kinetics in contrast to their silica counterparts. The enhanced performance can be primarily ascribed to the presence of aluminium within the material. The study discerned that the CO_2 adsorption performance on wet-grafted materials is constrained by diffusion, with this limitation being more pronounced at lower adsorption temperatures. Specifically, at 25 °C and 50 °C, the diffusional constraints are notably more conspicuous in wet-grafted Si-MCM-41 materials compared to their wet-grafted Al-MCM-41 counterparts. The reduced CO_2 adsorption performance and diffusional restrictions observed in wet-grafted Si-MCM-41 materials are attributed to structural degradation induced by exposure to steam. As a result of steam treatment, Si-MCM-41 materials displayed a substantial reduction in surface area, in stark contrast to the stability and performance retention observed in Al-MCM-41 materials.

A study carried out by Wang et al. [63]discusses the enhancement of CO_2 adsorption capacity using amine-grafted mesoporous silica SBA-15 by incorporating boron into its framework and subsequently removing it via acid treatment to increase the surface hydroxyl groups. The removal of boron creates silanol nests within the SBA-15 structure, each containing four silanol groups as seen in Fig. 24 This acid-treated boron-doped SBA-15 demonstrates higher silanol density and amine loading post-grafting compared to conventional methods.

The study reveals that these silanol nests can effectively graft amines and interact directly with CO_2, resulting in more than doubling the CO_2 adsorption capacity, particularly suitable for direct air capture. Furthermore, the acid-treated sample exhibits significantly higher silanol density and amine loading, leading to enhanced CO_2 adsorption capacities from low concentration streams like flue gases and ambient air. The adsorption capacity increases with temperature, making it appealing for CO_2 capture in warmer climates, and the stability of the material was confirmed through multiple adsorption and desorption tests. In a similar study by Ref. [147] it was revealed that Vinyltrimethoxysilane (VTMS)-treated SBA-15 adsorbents showed superior

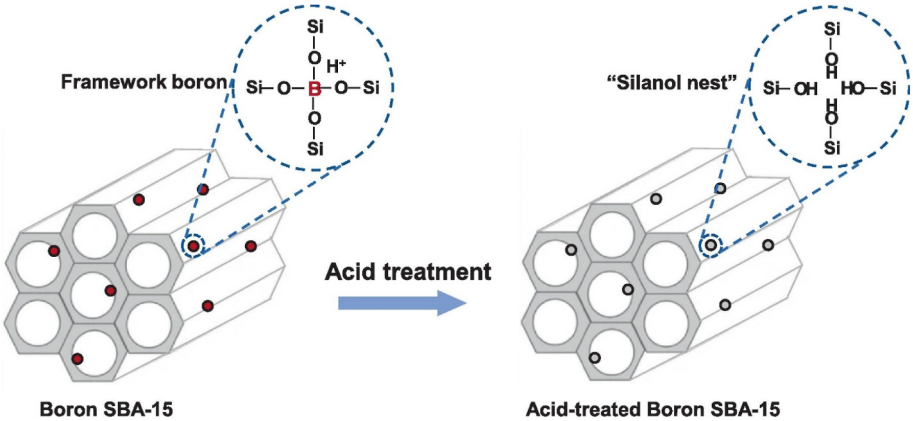

Fig. 24. Illustration for formation of "silanol nest" in acid-treated boron SBA-15 [63].

CO_2 uptake compared to untreated SBA-15 and Hexamethyldisilazane (HMDS)-treated variants, with the boron-doped, VTMS-treated, acid-etched sample achieving the highest amine efficiency (up to 0.28 mol CO_2/mol N). Enhanced CO_2 uptake was attributed to improved PEI-support surface interactions. In terms of stability, VTMS-treated supports were significantly more durable than HMDS-treated SBA-15, with the boron-doped sample exhibiting minimal PEI mass loss in aging tests, demonstrating excellent stability under humid conditions for DAC applications.

Taheri et al. [148] carried out surface modification of a support sorbent structure through a two-step preparation of halloysite nanotubes (HNTs) resulting in an enhanced mesoporous silica nanotube (EMSNTs). The resulting EMSNTs was observed to possess more than 8.5-fold increase in the specific surface area and 3.2-fold increase in the pore volume when compared to HNTs. This provided for more amine active sites for the adsorption of CO_2 when it was functionalized with TEPA leading to an increase of about 20−40 % in the capture rate by compared to PEI functionalization. Also, the as-prepared nanocomposite adsorbents demonstrated good reversibility and great thermal stability during the 12 cycles of adsorption−desorption. Bai et al. [149] studied the pivotal significance of pore structure in dictating adsorption characteristics. The study involved the fabrication of various MCF materials, varying in pore sizes and volumes, utilizing both calcination and ethanol extraction techniques to template removal. Subsequently, these MCF materials were subjected to wet grafting with triamine. The investigation into the adsorption performance of these MCF-based sorbents revealed that the pore volume and pore diameter of MCFs play a crucial role in determining CO_2 adsorption capacity and kinetics at ambient temperatures. Notably, larger pore sizes and volumes were observed to augment amine density on the MCF surface, consequently intensifying amine-wall interactions and steric hindrance. This enhancement, in turn, bolstered thermal and cyclic stability as a result of the intensified amine-wall interaction, exemplified by the absence of adsorption losses during cyclic adsorption-desorption trials as seen in Fig. 25. Similar observations on the effect of pore size and structure was reported by Ref. [150].

4.8. Effect of amine oxidation on CO_2 adsorption and cyclic stability

This section examines the impact of oxidation duration, temperature, and oxygen concentration on the stability of amine-supported materials for CO_2 capture. A study carried out by Ref. [151] underscored the complex interplay of factors influencing the stability and performance of TEPA-supported materials in CO_2 capture applications. In the study, it was revealed prolonged oxidation and higher temperatures lead to significant degradation, particularly with higher TEPA content. For instance, TEPA10/MF retained 95 % of its capacity after 5 h of exposure to O_2, while TEPA70/MF retains only 32 %. Higher TEPA content exacerbates degradation, rendering amino groups less effective for CO_2 capture, while higher temperatures accelerate degradation as TEPA10/MF retains 87 % of its initial CO_2 adsorption capacity after 18 h at 100 °C, while TEPA70/MF retains only 8 %. Furthermore, exposure to air, 5 % O_2, or pure O_2 lowered CO_2 capture abilities due to oxidative degradation. Pure O_2 caused the most significant loss. The degradation mechanism as seen in Fig. 26 involves free radical formation initiated by triggers like thermal fluctuation during the O_2 reaction with amines [152]. Also, higher amine content decreases O_2 diffusion rates yet increases sensitivity to oxidative conditions. Characterization techniques demonstrate reduced CO_2 adsorption due to organic content loss, accumulation of new products in pores, and surface oxidation [153, 154].

In another study conducted by Vu et al., [155] which aimed to investigate the stability of polyamine-based adsorbents to gas impurities for CO_2, it was noted that when TEPA adsorbent was subjected to oxidative treatment at low temperatures (60 °C) with 1 % O_2, the TEPA adsorbent experiences only a 1 % decrease in CO_2 adsorption capacity. However, at higher temperatures (80–100 °C) in pure O_2, significant capacity loss is observed as seen in Fig. 27, rendering the adsorbent ineffective after treatment at 100 °C for 18 h. Kumar et al. also reported the same observation [156]. The presence of O_2 in the gas stream reduces the adsorbent's lifespan, particularly at higher O_2 concentrations. Interestingly, the addition of CO_2 along with O_2 enhances the adsorbent's oxidative stability. This phenomenon which was also observed by Rosu et al. [157] is attributed to the rapid reaction between amino groups and CO_2, forming carbamate and protonated amine, which exhibit superior oxidative stability.

4.9. Effect of H_2S on CO_2 adsorption and cyclic stability

Research conducted by multiple scholars, including references [150–158], suggests that several factors, including chemical adsorption mechanism for CO_2 (zwitterion formation) and H_2S (proton transfer), H_2S acidity and interaction strength, amine type, moisture, H_2S concentration, and temperature, significantly influence the selectivity between H_2S and CO_2. One of the pioneering studies on the competitive adsorption of CO_2 and H_2S was conducted by Belmabkhout et al. [158]. They investigated the use of triamine-grafted pore-expanded mesoporous MCM-41 silica (TRI-PE-MCM-41) as an adsorbent for

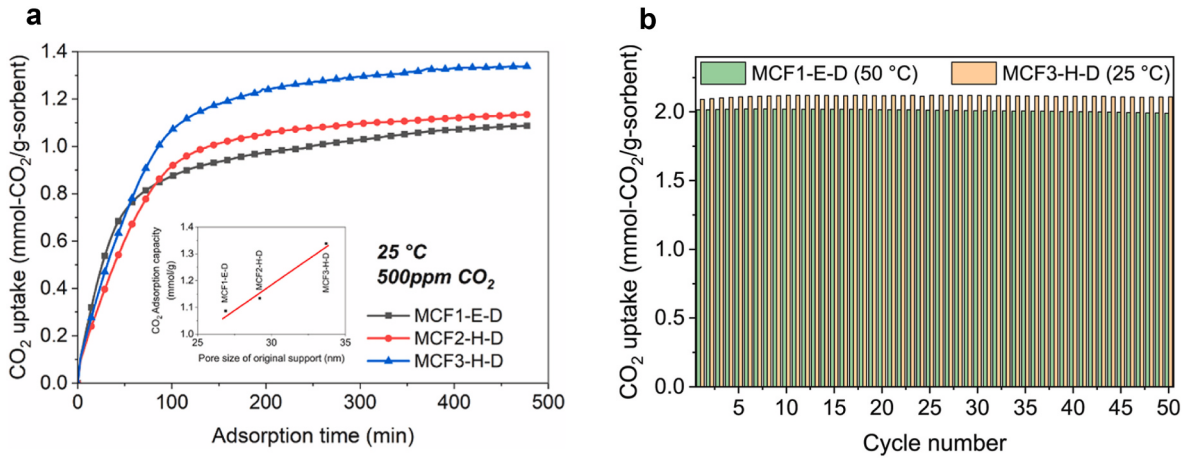

Fig. 25. (a) Depicts the CO_2 adsorption profiles of amine grafted MCFs in ambient air streams containing 500 ppm CO_2 at 25 °C, illustrating the impact of pore size on CO_2 adsorption. (b) Shows the results of a cyclic adsorption-desorption test conducted on MCF1-E-D (at 50 °C) and MCF3-H-D (at 25 °C) under a gas mixture of 15 % CO_2 in N_2 [149].

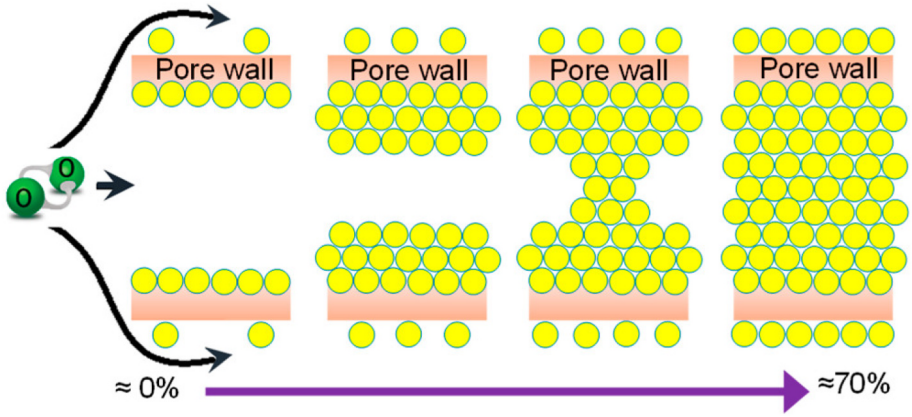

Fig. 26. A depiction of agglomerated amine molecules within pores and on the surface of silica, with varying amine loadings ranging from 10 to 70 wt% [151].

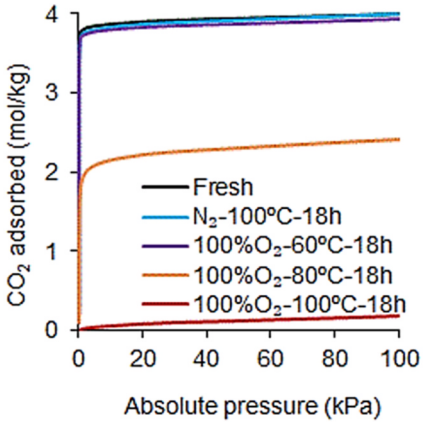

Fig. 27. Impact of oxidation temperature on TEPA adsorbent stability [155].

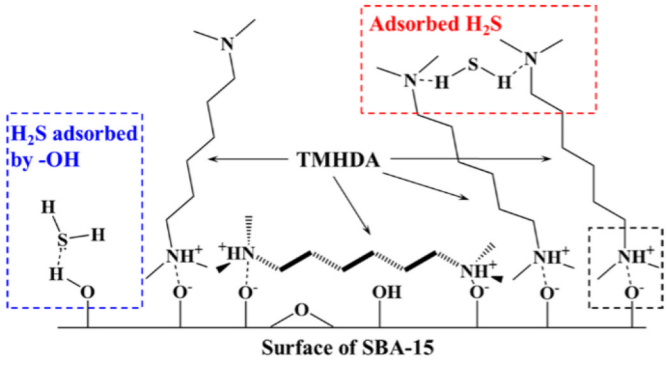

Fig. 28. Suggested sorption mode of H_2S on TMHDA/SBA-15 [160].

simultaneous removal of CO_2 and H_2S. The study revealed that at lower H_2S concentrations, H_2S exhibited preferential adsorption over CO_2, with H_2S/CO_2 selectivity reaching as high as 68 %. However, as the H_2S concentration increased, the selectivity of H_2S over CO_2 decreased, particularly within the temperature range of 25–50 °C. This phenomenon was attributed to differences in the formation of CO_2 zwitterions compared to the proton transfer of H_2S, as well as the higher propensity of H_2S for physisorption compared to CO_2. In a similar study conducted by Jaiboon et al., [159], it was observed that at lower temperatures (30 °C–50 °C), H_2S is easily regenerated in comparison to CO_2 due to its lower acidity and weaker interaction strength. The impact of amine type on H_2S/CO_2 competitive adsorption was highlighted in a study by Quan et al., [160]. Among the sorbents, TMHDA/SBA-15 with tertiary-amine exhibited selective H_2S removal even at high CO_2 concentrations (10–40 vol%). Optimal H_2S sorption capacities were achieved with a 15 wt% TMHDA loading, forming a monolayer of TMHDA on the support surface, with physisorption contributing to the overall capacity as illustrated in Fig. 28.

While introducing CO_2 had a negative impact on sorption for primary and secondary amines, TMHDA/SBA-15 maintained 90 % of its capacity even at 40 vol% CO_2. The sorbent could be regenerated at mild conditions (110 °C) and exhibited stable sorption performance. The research conducted by Okonkwo et al. [161] further supports the previously mentioned finding of Quan et al., [160,162] regarding the role of amine structure in capturing H_2S from dilute streams using solid adsorbents. The study investigated three amine-modified SBA-15 adsorbents with similar amine loadings for H_2S adsorption at different temperatures and concentrations. SBA-15_MAPS had the highest H_2S uptake of 0.16 mmol H_2S/g sorbent, while SBA-15_DMAPS had lower adsorption of 0.055 mmol H_2S/g. SBA-15_APS showed moderate H_2S uptake of 0.13 mmol/g. Although SBA-15_MAPS had the highest capacity, it exhibited less stability compared to SBA-15_DMAPS, which showed better cyclic stability with 5 % capacity loss between cycles 2 and 4 as against 12 % for SBA-15_MAPS. Analysis of adsorption isotherms and heats of adsorption indicated that SBA-15_MAPS, with secondary amines, was more efficient in capturing H_2S at low concentrations due to its higher reaction heat. On the other hand, SBA-15_DMAPS, with tertiary amines, may be more effective for H_2S adsorption at higher concentrations. In the study conducted by Okonkwo et al. [163], the potential of amine functionalized sorbents for H_2S removal, particularly in humid conditions, is emphasised. The research investigates the sorption of H_2S on solid-supported amines under both dry and humid conditions. It is observed that humidity promotes the formation of chemisorbed species, thereby enhancing the sorption capacity for H_2S. The authors attributed the enhanced selectivity of H_2S over CO_2 by the adsorbent to influence of kinetic factors. De Sousa et al. [164] investigated how H_2S and H_2O affect CO_2 capture using amine-functionalized silicas and reported that H_2S competes with CO_2 and blocks amine groups, hindering CO_2 adsorption. An illustration of the mechanism is shown in Fig. 29.

Anyanwu et al. [165] also investigated the effect of humidity in amine functionalized SBA-15 to CO_2 capture and natural gas desulfurization. Conventional and pore expanded SBA-15 were amine-grafted under dry and wet conditions using N-(3-trimethoxysilylpropyl)diethylenetriamine. The findings indicate that high amine loadings and lower temperatures enhance H_2S adsorption. Unlike CO_2, the maximum H_2S adsorption capacity decreased from 25 to 50 °C for conventional and pore expanded SBA-15 containing 0.6 mL of water, and further temperature increases resulted in negligible H_2S adsorption. It is suggested in the study that H_2S adsorption is predominantly thermodynamically

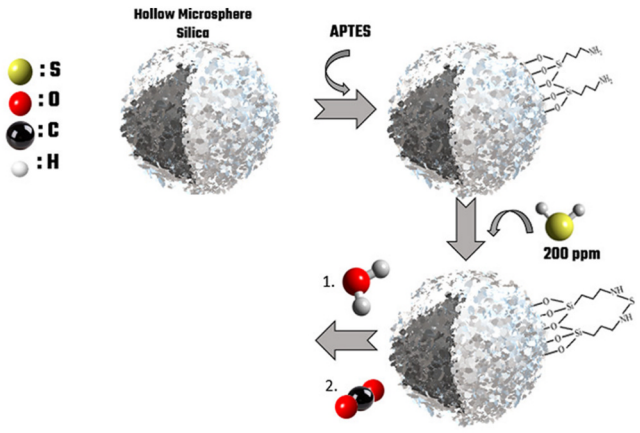

Fig. 29. Suggested mechanism of H_2S saturation in silica materials functionalized with amines [164].

controlled, as the estimated kinetic barrier for H_2S diffusion from the adsorbent surface into the bulk amine is approximately three times lower than that of CO_2.

4.10. Effect of NOx on CO_2 adsorption and cyclic stability

Multiple studies have demonstrated that NO and NO_2 can impact the CO_2 adsorption capacity in amine-functionalized silica adsorbents, with the adsorbents exhibiting a greater affinity for NO_2 than NO. This observation is attributed to the higher polarity and acidity of NO_2 in comparison to NO. Razaei et al. [166] carried out a study which highlights the importance of primary amines with high amine loadings for NO adsorption, as well as emphasizing the impact of NO_2 on CO_2 adsorption by aminosilica sorbents. The study aimed to assess the irreversible binding of SO_2, NO, and NO_2 to aminosilica adsorbents. The adsorbents used in the study were created using poly(ethyleneimine) and three distinct silane coupling agents containing primary, secondary, and tertiary amines, all based on propyltrimethoxysilane linkers. Findings show that adsorbents with primary amines demonstrated a stronger affinity for NO compared to secondary and tertiary amines. However, the overall adsorption capacity for NO on the aminosilica adsorbents was low (below 0.07 mmol of NO/g). Conversely, all adsorbents exhibited high adsorption capacity for NO_2, leading to a significant reduction in CO_2 capacity due to irreversible binding and subsequent amine deactivation.

In a further study, Rezeai et al. [167] focused on packed bed breakthrough experiments involving amine-impregnated and amine-grafted silica adsorbents for CO_2 adsorption. The stability of these adsorbents in real flue gas conditions was investigated by examining their performance in the presence of NOx impurities. Coadsorption experiments with NO and CO_2 showed that NO had minimal interaction with the amine-based adsorbents, leading to unaffected CO_2 capture. Further tests and cycles confirmed the absence of negative effects between NO and CO_2, indicating stable CO_2 adsorption even in the presence of NO. Razeai et al. [167] conducted single-adsorption experiments using high NO_2 concentrations and found simultaneous breakthrough with CO_2. Coadsorption experiments with realistic conditions (20 ppm NO_2 and 10 % CO_2) showed that NO_2 concentrations below 20 ppm had minimal impact on aminosilica adsorbent stability for CO_2 capture as seen in Fig. 30.

However, prolonged exposure to NO_2 resulted in a significant decrease in CO_2 adsorption capacity. Similar observation was made by Meng et al. [78] and Li et al. [168], and the phenomenon was attributed to the formation of heat-stable acid adducts and, likely, N-nitro ($N–NO_2$), C-nitroso (C–N═O), and C-nitro ($C–NO_2$) compounds which aid irreversible adsorption.

4.11. Effect of SOx on CO_2 adsorption and cyclic stability

The presence of moisture, concentration of SO_2, adsorption temperature, amine loading, and type of amine have been identified as factors that influence the selectivity of SO_2 over CO_2. The effect of SO_2 concentration on the adsorption capacity of different adsorbents was investigated by Rezeai et al. [166]. The study revealed that higher SO_2 concentrations between 100 ppm–200 ppm led to increased SO_2 capacities of 0.79 and 1.08 mmol of SO_2/g, with secondary amines (MAPS) exhibiting the highest affinity for SO_2. Exposure to SO_2 resulted in a loss of CO_2 capacity due to irreversible adsorption of SO_2 on the amine sites, reducing the available amine sites for CO_2 adsorption. Increasing the temperature from 35 °C to 75 °C decreased the SO_2 adsorption capacity, while the CO_2 capacity was less affected. The amine loading had a linear relationship with SO_2 equilibrium capacity, and higher amine contents resulted in higher capacities. Secondary amine adsorbents displayed higher amine efficiency, while PEI-impregnated adsorbents showed diffusion-limited SO_2 adsorption at higher amine contents. Similar observation was reported by Hallenbeck et al. [169]. Tailor et al. [163–165] reported that the presence of water vapor significantly increased the adsorption capacity, with a 3-fold increase observed under 19 % relative humidity. Also, the saturation capacity of SO_2 increased with higher concentrations of SO_2, while its adsorption capacity decreases with Increasing temperature indicating a thermodynamically

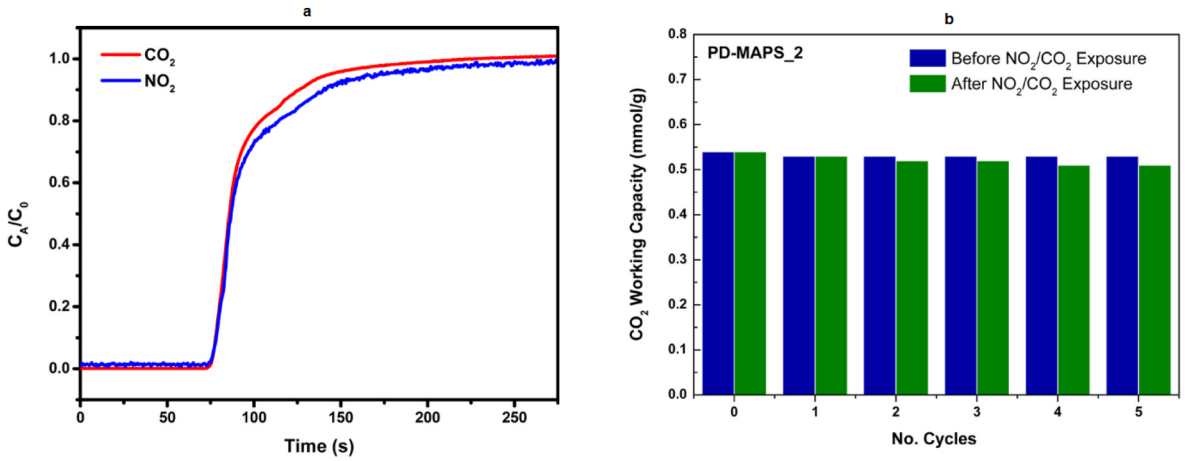

Fig. 30. (a) Coadsorption breakthrough profiles for CO_2 and NO_2 on amine-functionalized after exposure to 20 ppm of NO_2/10 % CO_2 at 35 °C. (b) CO_2 working capacity of amine-functionalized materials before and after exposure to 20 ppm of NO_2/10 % CO_2 at 35 °C [167].

controlled process. Regeneration experiments showed a decrease in working capacity after a few cycles, primarily attributed to evaporation of impregnated amine rather than amine deactivation. The coadsorption behaviour of SO_2 and CO_2 on amino silica adsorbents was examined by Rezeai et al. [167]. In this study, the adsorbents were exposed to a gas mixture containing 200 ppm SO_2 and 10 % CO_2 at 35 °C, and breakthrough profiles of CO_2 and SO_2 were measured. As seen in Fig. 31, CO_2 broke through the bed faster than SO_2 due to its higher concentration. Irreversible binding of SO_2 to specific amine sites caused a decrease in capacity over cycles. However, higher adsorption temperatures led to earlier breakthrough of SO_2 and reduced adsorption capacity. In simultaneous adsorption, NO and CO_2 quickly breakthrough, while SO_2 is trapped. The loss of CO_2 capacity is mainly due to SO_2, not NO, with no synergistic interactions observed.

Lui et al. [170] studied the effect of SO_2 concentration and adsorption temperature on CO_2 adsorption TEPA-impregnated MCM-41 as a reference. The CO_2 adsorption capacity increased with increasing temperature from 293 to 333 K and then decreased at 353 K. Cyclic adsorption/desorption behaviour showed that the CO_2 adsorption capacity decreased after exposure to various SO_2 concentrations (100, 200, 500,1000, and 2000 ppm) and declined further after multiple cycles, likely due to a decrease in accessible adsorption sites and the accumulation of sulphate/sulphite species moreover, similar observation was recorded by AlQahtani et al. [171] and Narayanan et al. [172]. Fan et al. [173] showed that secondary amine fibre material (CA-S-MAPS), could offer higher resistance to SO_2 deactivation compared to primary amine fibre material as seen in Fig. 32.

The initial stage of cyclic operation shows a more rapid reduction in CO_2 capacity for primary amine (CA-S-APS). Differences in SO_2 degradation may be attributed to the variation in adsorption sites and the reaction mechanism. The interference was attributed to the irreversible binding of SO_2 and NO_2 with amines, leading to the degradation of PEI/SiO_2. Li et al. [168] studied the effects of O_2, SO_2, and NOx on branched and linear polyethyleneimine (PEI) functional silica CO_2 adsorbents (BPEI-SiO_2 and LPEI-SiO_2) were investigated. O_2 was found to significantly oxidize BPEI-SiO_2, leading to a 23.0 % decrease in CO_2 adsorption capacity, while LPEI-SiO_2 showed only a 3.6 % decrease. SO_2 caused severe degradation of both adsorbents, resulting in significant losses in CO_2 adsorption capacity. NO_2 and NO had minimal impact on CO_2 adsorption capacity but caused degradation of the adsorbents.

Accordingly, it is seen that asides from urea formation, the presence of impurities such as H_2S, SOx and NOx, the type of amine and its properties, method of functionalization, and sorbent support structure

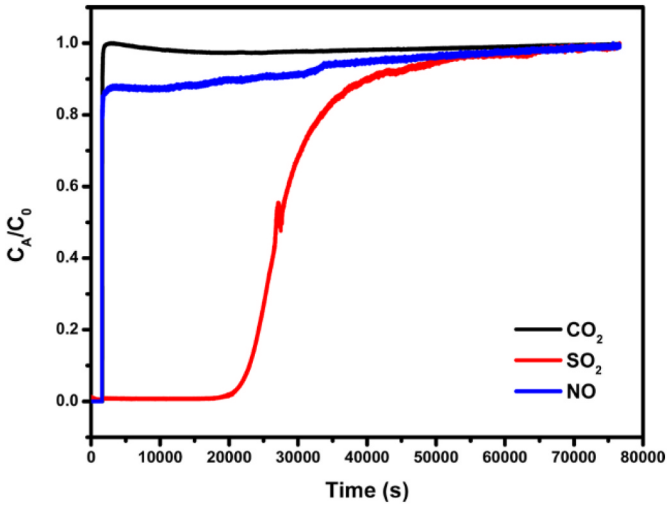

Fig. 31. Adsorption breakthrough profiles for CO_2, SO_2 and NO_2 on amine functionalized adsorbent after exposure to 200 ppm of SO_2/200 ppm of NO/10 % CO_2 at 35 °C [167].

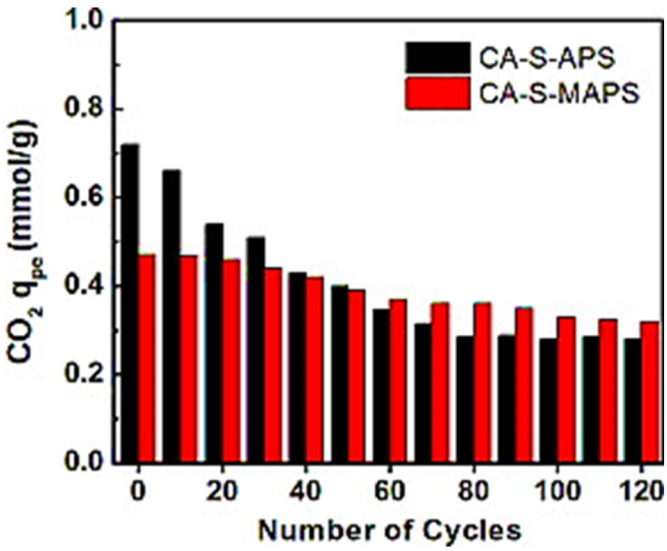

Fig. 32. Comparison of CO_2 capture capacity in primary amine fibre material (CA–S–APS) and secondary amine fibre material (CA–S–MAPS) adsorbents when exposed to dry flue gas with 200 ppm SO_2 [173].

all contribute to the thermal and cyclic stability of AFA. Studies have shown that the formation of urea can be greatly impaired in presence of moisture by increase in amine loading which leads to more water molecules being adsorbed and bicarbonates being formed which are reversible. Eqs. (1) and (2) show that in the presence of a water molecule, 1 mol of amine is needed to adsorb 1 mol of CO_2 to form bicarbonate, as against 2 mol of amine needed to adsorb 1 mol of CO_2 in the dry condition to form carbamate. This further explains why AFA perform better in wet conditions than in dry conditions [174].

$$2(RNH_2) + CO_2 \leftrightarrow RNHCO_2^- RNH_3^+ \quad (1)$$

$$RNH_2 + CO_2 + H_2O \leftrightarrow RNH_3^+ HCO_3^- \leftrightarrow RNH_3^+ CO_3^{2-} \quad (2)$$

Although formation of bicarbonates improves the cyclic stability when compared with urea formation, it still does not make AFA economically viable because the reversibility of bicarbonate in the long run leads to the cyclic instability of AFA after operating for a couple of adsorption-desorption cycles far less than a thousand. Despite the improvement noticed in the thermal and cyclic stability by these factors, the challenge of achieving thousands of cycles before disintegrating persist. Furthermore, these factors that contribute to improvement of thermal and cyclic stability have shown that a balance needs to be achieved between improved thermal/cyclic stability and adsorption capacity. In the works carried out by Refs. [25,112,126,132,139, 143–145] it is seen that application of any of the contributing factors to improved thermal and cyclic stability causes a decline in the CO_2 adsorption capacity of the AFA. The decrease in CO_2 adsorption capacity is attributed to an increase in surface resistance at the adsorption sites offered to the diffusing CO_2 molecules. Since the adsorption phenomenon carried out at the gas-solid interface of the adsorbent is propelled by diffusion, then an understanding of the host-guest interaction with respect to diffusivity and surface resistance becomes paramount and should be studied.

Reviewed literatures in this section underscore the fact that thermal and cyclic stability of AFA for CO_2 capture is subject to a multitude of interrelated factors. The choice of functionalization method, conversion of primary amines to secondary amines, double functionalization approaches, and the utilization of mixed polyamines play pivotal roles in enhancing stability and adsorption capacity. Moreover, factors such as amine volatility, molecular weight, support morphology, and textural properties significantly influence the overall performance of AFA

materials. The incorporation of secondary amines, alteration of support morphology through doping, and the strategic selection of amine types and mixtures are paramount in mitigating thermal degradation and improving cyclic stability. Additionally, the impact of oxidation, impurities such as H_2S, NOx, and SOx, as well as amine volatility, underscores the necessity for comprehensive understanding and meticulous optimization of AFA materials. Therefore, efforts towards enhancing stability and performance must consider the complex interplay among these factors.

5. Host-guest interaction in silica-based amine functionalized adsorbents

Within the domain of silica-based AFA, the term "host-guest interaction" defines the chemical bonding between the adsorbent material (referred to as the host) and the molecules or ions (referred to as the guests) being adsorbed or extracted from a liquid or solution. Silica-based AFA are meticulously engineered to exhibit a heightened degree of selectivity in their capacity to adsorb or interact with target guest molecules through diverse chemical mechanisms. This phenomenon is frequently described as "host-guest interaction." These interactions encompass a range of mechanisms, including chemical adsorption, where amine groups can establish chemical bonds or reactions with specific functional groups on the guest molecules, physical adsorption, which involves non-covalent forces such as van der Waals interactions and hydrogen bonding, and ion exchange, where amine groups may engage in ion swapping with the guest molecules. The subsequent section offers an overview of research endeavours that delve into the intricate facets of these interactions.

5.1. Amine – CO_2 interaction in silica-based amine functionalized adsorbents

A research study conducted by Yoo et al. [175] furnishes direct evidence supporting intramolecular CO_2 capture within individual silane molecules, thus elucidating the intricate interplay among amines, CO_2, and surface silanols for grafted amine sorbents. Four distinct amine-containing organosilanes, specifically propylamine (MONO), propylethylenediamine (DI), propyldiethylene-triamine (TRI), and propyltriethylenetetramine (TREN), are employed to modify mesoporous silica.

The silanes are assessed for their CO_2 adsorption capacity, and the presence of silanol groups on the surface is variably preserved or capped, allowing for comparative analysis. The study's findings reveal that as the number of amines in the silane molecule increases (MONO < DI < TREN ~ TRI), the efficiency of silane molecules in terms of CO_2 adsorption is augmented, primarily owing to their ability to intramolecularly capture CO_2. Furthermore, it is observed that silanols on the surface contribute to a collaborative CO_2 uptake process as proposed in Fig. 33, illustrating interactions among amine, CO_2, and silanol, which represents the principal mode of sorption for the MONO material. Moreover, the presence of multiple amines within a single silane molecule amplifies intramolecular CO_2 capture, consequently elevating the measured heat of adsorption. In the context of impregnated amines like PEI/TEPA, Moon et al. [176] noted that the hydrophilic sections of SBA-15 surfaces, housing mildly acidic silanol groups, attract PEI/TEPA, potentially impeding CO_2 capture. This results in a diminished effectiveness of amines located near the supporting surface for CO_2 capture as illustrated in Fig. 34.

The mobility of amines in PEI/SBA-15 sorbents can be influenced by humidity, which affects their CO_2 capture capacity. Moon et al. [177] showed that under dry conditions, PEI becomes less mobile due to water removal, resulting in reduced CO_2 diffusivity and slower uptake rates over cycling. In contrast, humid conditions increase PEI mobility by acting as a lubricant, allowing for faster CO2 diffusion and improved uptake rates. Higher humidity further enhances PEI mobility, maintaining open pore spaces and supporting better CO_2 capture performance across cycles.

Vallace et al. [178] conducted research that highlights the relationship between CO_2 uptake, pseudo-equilibrium capacity, and diffusion rates of supported amines. Their study also explored how CO_2 interacts with wall-bound and plug-like structures at different concentrations. It was observed that the plug-like PEI motifs experience fewer forces in general compared to the wall-bound motifs. This outcome is attributable to the fact that the surface area of a plug is minimized due to surface tension, as plug-like PEI domains predominantly interact with themselves through base-base interactions, leading to geometries that minimize surface area. In contrast, the additional pore-wall forces exerted by the wall-bound motifs, including hydrogen bonding and acid-base interactions, override the base-base interactions, ultimately resulting in a higher surface area for the wall-bound control volume, accompanied by a higher amine site surface density. Differences in PEI morphology among samples with varying PEI loadings impact the observed reaction rate constant. Specifically, an increase in PEI loading did not consistently result in a corresponding rise in the reaction rate constant.

In a study aimed at investigating the distribution and mobility of amine supported SBA-15, Moon et al. [142] harnessed the power of 1H T1−T2 correlation NMR (Nuclear Magnetic Resonance) experiments to illuminate the structural and dynamic attributes of TEPA and PEI supported within the SBA-15 framework and to elucidate their correlation with CO_2 sorption profiles. The NMR analysis revealed that TEPA exhibited a discernibly more diffuse NMR signal within the pore-coating domain as opposed to PEI, and this disparity was ascribed to the distinct chain topologies of these two amine variants. TEPA was inferred to engage in monodentate or bidentate binding interactions, while the branched configuration of PEI led to the formation of multidentate associations with the silica surfaces. At intermediate amine loadings,

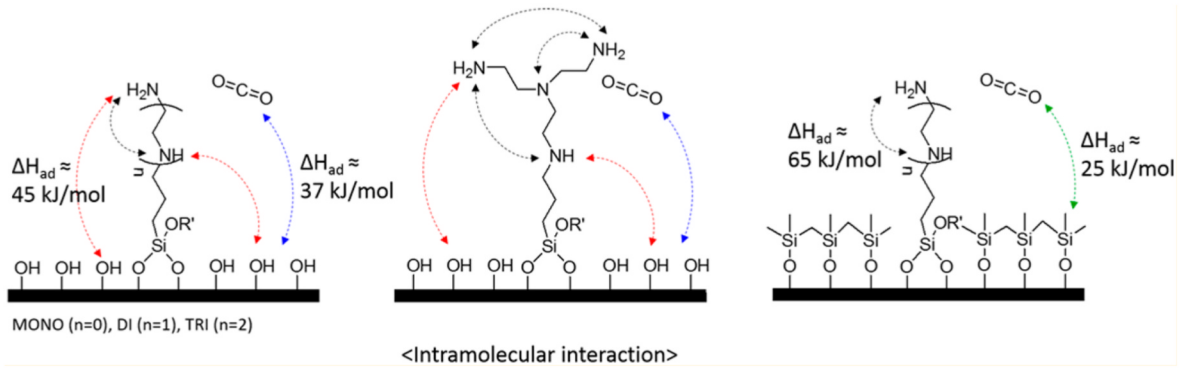

Fig. 33. Illustration on collaborative CO_2 adsorption by surface sianols [175].

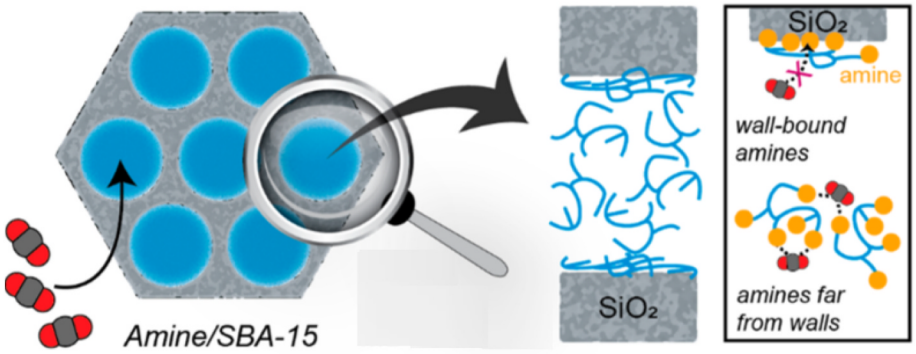

Fig. 34. Illustration on mobility of confined PEI in SBA-15 and effects of wall−PEI interactions [176].

approximately 60 % of TEPA exhibited heightened mobility of pore-coating TEPA entities. In contrast, this heightened mobility was less conspicuous in the case of PEI, potentially due to the greater impediments posed by the multiple arms of PEI molecules tethered to the surface. As the composite materials approached full saturation with amines (pore fill fraction ~100 %), both TEPA and PEI displayed a substantial augmentation in molecular mobility (see Fig. 35). This intriguing observation indicated that nearly saturated pores facilitated spin coupling and spin diffusion, emblematic of an intensified molecular mobility within the sorbent [142].

In a study carried out by Wilfong et al. [179] the diffusion of CO_2 was investigated during concurrent desorption and readsorption processes on silica and TEPA/silica sorbents, it was noted that slow CO_2 uptake and desorption can be attributed to the intricacies of CO_2 diffusion through the intricately woven network formed by CO_2 molecules adsorbed within the pores of the amine/silica sorbents, coupled with the phenomenon of readsorption of CO_2 at the amine sites situated within the pores as well as at the external surfaces of the sorbents. It is worth noting that the efficacy of CO_2 adsorption and desorption hinges on sorbent materials featuring a low amine density at their external surfaces and pore openings.

The role water plays during amine-CO_2 interaction was highlighted in a work carried out by Chen et al. [180] where distribution and transport of CO_2 within the HB-PEI-loaded MCM-41 system, focusing on the self-diffusion coefficient ($D(CO_2)$) was investigated. Force field parameters, developed using DFT modelling, were used to describe interactions among CO_2, H_2O, HB-PEI, and MCM-41. Optimal HB-PEI loading, determined at approximately 34 wt%, fully covered the MCM-41 pore surface. The study found that H_2O molecules dominated molecular adsorption due to their affinity with silanol groups on MCM-41 and amine groups in HB-PEI. Consequently, the distribution of H_2O was insensitive to HB-PEI variations. $D(CO_2)$ in the PEI/MCM system was significantly lower than in pure HB-PEI due to CO_2's attractive interaction with silanol groups on MCM-41. However, $D(CO_2)$ increased with 34 wt% HB-PEI content, as more CO_2 molecules became associated with the HB-PEI phase. $D(H_2O)$ in the PEI/MCM system was lower than in pure HB-PEI but increased with H_2O concentration. The presence of H_2O enhanced CO_2 capture in the HB-PEI-loaded MCM-41 by increasing CO_2 correlation with amine groups and facilitating bicarbonate formation. In another study carried out by Moon et al. [181] the influence of various interaction types between mesoporous SBA-15 walls and PEI on the dynamics and morphology of PEI was investigated.

To achieve this the chemical properties of the pore walls were tailored by modifying them with alkoxysilanes featuring different end groups, affecting their interaction with the amine groups of PEI as shown in Fig. 36. Initially, it was expected that less attractive walls would lead to faster PEI dynamics. Surprisingly, the least attractive, repulsive case resulted in lower PEI mobilities compared to a moderately attractive case. Advanced techniques such as QENS, T1−T2 NMR, and MD simulations provided insights into the molecular-level phenomena occurring

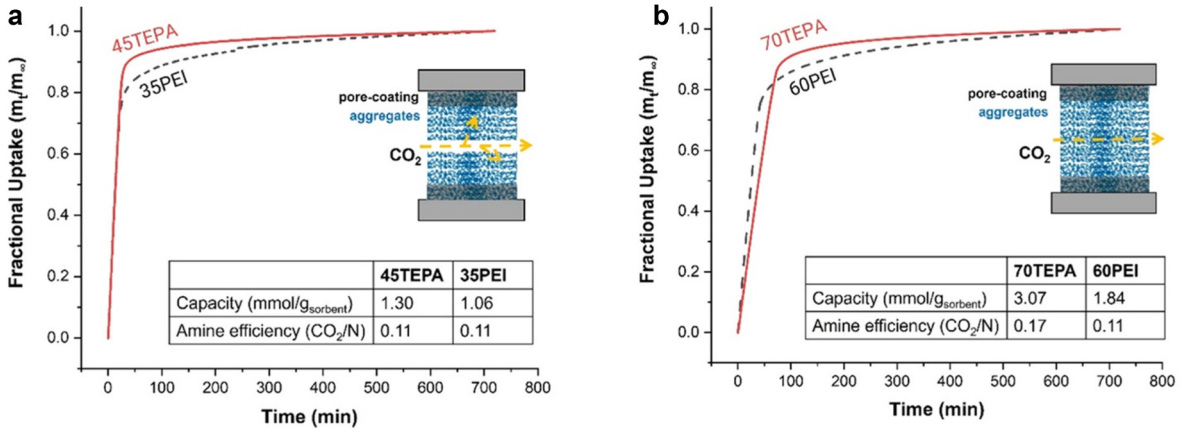

Fig. 35. (a) Fractional CO2 uptake curves for intermediate weight loadings of TEPA and PEI (45TEPA and 35PEI). (b) Fractional uptake curves for composites containing amine compounds effectively occupy the void volume within pores (70TEPA and 60PEI) [142]Furthermore, these NMR findings were thoughtfully juxtaposed with CO_2 uptake profiles. Materials with relatively lower amine content, exemplified by 20TEPA and 20PEI, demonstrated reduced amine efficiency owing to the enclosure of amines near the pore walls as illustrated in Fig. 34. In contrast, intermediates, and high amine loadings (45−70TEPA and 35−60PEI) exhibited elevated amine efficiency, plausibly due to the presence of a greater number of amine aggregates. The investigation also unearthed a clear nexus between faster amine mobility and accelerated CO_2 uptake. However, materials laden to near repletion with amines exhibited a decelerated uptake, as pore congestion became apparent. Here, the cross-linking of amine groups, catalysed by CO_2, curtailed molecular mobility, providing insights into the complex interplay between amine structure, mobility, and CO_2 sorption phenomena.

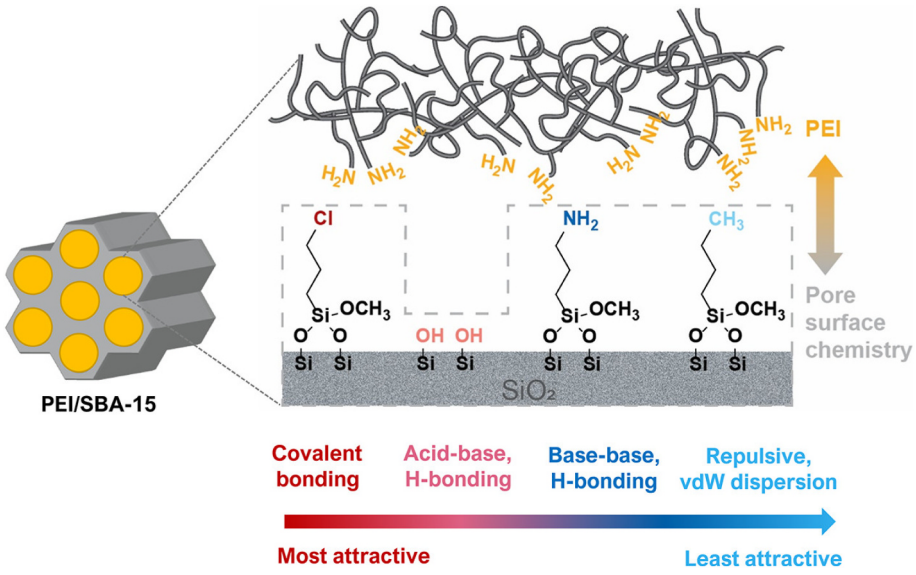

Fig. 36. Changes in the surface chemistries of the support and anticipated attraction levels between PEI and the pore surface [181].

at the solid/PEI interfaces, revealing that remaining silanol groups and the hydrophilic SiO_2 surface could still attract PEI chains, leading to unique PEI morphologies across different cases.

5.2. Surface chemistry of chemisorbed products during amine-CO_2 interactions

Seminal research on the detection of chemisorbed CO_2 products was conducted by Chen et al. [182,183], unveiling that the interplay between CO_2 and amino groups triggers chemical changes, specifically the creation of carbamates and bicarbonates. Carbamates arise from the interaction between a primary amine group (-NH_2) and CO_2, while bicarbonates form in the presence of water and are stabilized by adjacent ammonium propylsilane groups on the sorbent. In their research, Foo et al. [184] embarked on a study with the aim of unravelling the structural characteristics of adsorbed CO_2 on amine-grafted SBA-15 adsorbents. These adsorbents underwent specific modifications involving various aminosilanes, namely 3-aminopropyltrimethoxysilane (APS), N-methyl-3-aminopropyltrimethoxysilane (MAPS), and N, N-dimethyl-3-aminopropyltrimethoxysilane (DMAPS). Their findings unveiled distinct patterns among these variants. APS-SBA15 predominantly featured monocarbamic acid as the primary adsorbed CO_2 species, with stabilization occurring through hydrogen bonding with surface hydroxy groups. In contrast, MAPS-SBA15 displayed the presence of two distinct carbamic acid species: monomer and dimer.

These carbamic acid species found stability through dimer formation and interactions with adjacent NH groups, an effect attributed to the steric hindrance introduced by the additional methyl group in MAPS. However, both APS-SBA15 and MAPS-SBA15 exhibited the formation of carbamate species, although the species on APS-SBA15 displayed lower asymmetry and higher concentrations compared to MAPS-SBA15. DMAPS-SBA15 primarily exhibited the formation of bicarbonate species, indicating variations in species formation attributed to disparities in amine functional groups and their associated steric hindrance. Outcome of this study introduced carbamic acid as a potential chemisorbed CO_2 specie. Fig. 37 illustrates suggested structure of carbamic acid formed on AFA. This finding was affirmed in a study by Chen et al. [185] where the focus was on probing the interaction between amine-functionalized materials, specifically MAPS/SBA15 and APS/SBA15, with water and CO_2. The primary objective was to gain insights into how humidity and surface chemistry influence these interactions. These reactions involved the utilization of both primary

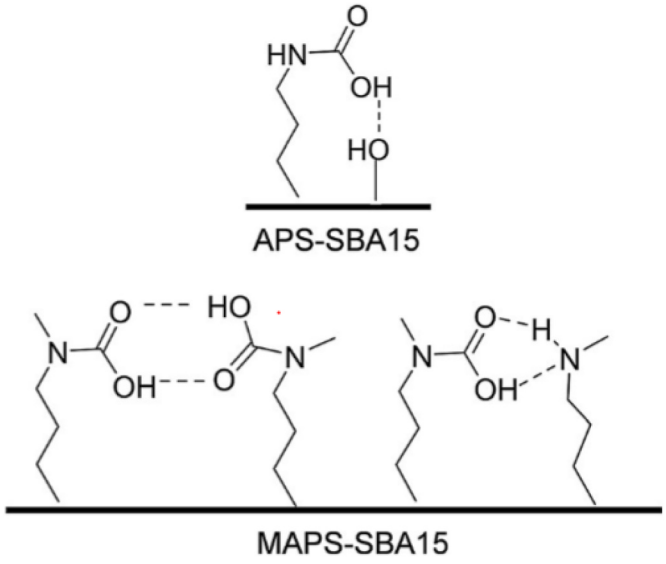

Fig. 37. Hypothetical configurations of carbamic acid generated on APS-SBA15 and carbamic acid dimers formed on MAPS-SBA15 [184].

(APS) and secondary amine (MAPS) functionalized SBA15, resulting in the production of bicarbonate, carbamic acid, and methylpropylammonium pendant species. In the case of DMAPS-functionalized SBA15, the observation was the generation of bicarbonate and dimethylpropylammonium species. A particularly intriguing finding emerged from the 13C resonance of bicarbonate, which served as an indicator of CO_2's interaction with amine groups in the presence of water. Notably, for all the functionalized materials under scrutiny in this study, it was observed that at lower temperatures, the bicarbonate 13C signal manifested as distinct resonances. Importantly, this effect was found to be reversible with changes in temperature. Further investigations using 13C–1H HETCOR NMR experiments unveiled the presence of two discrete bicarbonate environments. One of these environments was associated with water residing on the walls of the mesoporous silica support, while the other bicarbonate environment was coordinated to water within the pore or the "mid-channel." Remarkably, these bicarbonate species retained coupling with the pendant amine moieties.

In Fig. 38, the displayed region is the area where chemisorption

products, namely carbamate, carbamic acid, and bicarbonate, are generated. Dotted blue lines appear at 162 and 168 ppm, aligning with the central points of bicarbonate resonances, while the range between them encompasses carbamate and carbamic acid. The continuous blue lines represent individual peak fits, and the red lines depict the cumulative result of all fitted peaks. The variation in chemisorbed species, as proposed by Lee et al. [186], can be attributed to the predominant influence of the amines' basicity on the chemistry of CO_2 capture in the presence of water. This comprehension provides valuable insights into the mechanisms of CO_2 capture in diverse scenarios.

Recently, a study carried out by Song et al. [187] has challenged the common understanding that bicarbonate forms under humid conditions. Their study investigated the host-guest interactions between amine groups and CO_2 in a benchmark amine-functionalized adsorbent, Lewatit® VP OC 1065, under controlled CO_2 and humidity conditions, using solid-state NMR spectroscopy. Key findings reveal that CO_2 adsorption involves the formation of ammonium carbamate and carbamic acid species at various CO_2 loadings. At low CO_2 partial pressures, only ammonium carbamate forms, but with increasing CO_2 pressure, carbamic acid also becomes prominent. Interestingly, physisorbed CO_2 is only observed at the highest tested CO_2 loading. The NMR analysis as shown in Fig. 39 indicates that bicarbonate does not form in the presence of water. Instead, humidity influences CO_2 adsorption capacity through physical effects: water causes the polymer to swell, increasing pore size and making more amine groups available for CO_2 capture. This swelling effect at moderate humidity levels (30 % RH) enhances adsorption capacity without altering the chemical pathway. However, at high humidity (80 % RH), excessive water adsorption blocks CO_2 adsorption sites, reducing capture efficiency. These findings suggest that the primary impact of water on CO_2 capture in this system is structural rather than chemical, highlighting a need for optimized humidity levels to balance adsorption efficiency and stability.

The research works discussed in this section has been able to shed light on the surface chemistry of chemisorbed products during amine-CO_2 interactions, mechanisms of CO_2 capture and the role of different amine-containing organosilanes in modifying mesoporous silica and their impact on CO_2 adsorption. These studies demonstrate the significance of intramolecular CO_2 capture within silane molecules, particularly how increasing the number of amines enhances CO_2 adsorption efficiency and emphasizes the importance of exploring host-guest interactions in silica-based AFA to understand the intricate chemistry underlying CO_2 capture processes. A strong host-guest interaction can enhance CO_2 capture efficiency by forming stable carbamate and carbamic acid species, which improve selectivity and adsorption capacity. However, excessively strong interactions can also lead to challenges, such as requiring higher energy for CO_2 desorption, which can degrade amine groups over multiple adsorption-desorption cycles, reducing the adsorbent's lifespan. Furthermore, host-guest dynamics influence the adsorbent's resilience under cyclic and thermal stress. Effective management of these interactions, possibly through tuning the amine type or distribution, can balance strong CO_2 binding with ease of regeneration. Optimizing these interactions enhances the adsorbent's thermal and cyclic stability, ultimately improving its feasibility for large-scale, long-term CO_2 capture applications. Additionally, the studies reveal the morphological differences between different amine motifs and their effect on the apparent reaction rate constants, providing a clear foundation for further research on optimizing AFAs. The study also highlighted the complexities of CO_2 diffusion, especially within amine-functionalized silica sorbents, explaining how slow CO_2 uptake and desorption are influenced by CO_2 diffusion through the sorbent's porous network, with readsorption occurring at amine sites. Studies investigating the interplay between amines and CO_2 highlight the crucial role of intramolecular CO_2 capture within silane molecules, enhancing CO_2 adsorption efficiency with increasing amine density. Importantly, these studies emphasize the need to manage amine density at external surfaces and pore openings to achieve efficient CO_2 adsorption and desorption. However, despite these significant advancements in knowledge, there are still gaps in our understanding of the precise mechanisms underlying the interaction between solid amines and CO_2. These gaps particularly relate to diffusional limitations and how the interaction between the guest (CO_2) and host (sorbent) at the sorbent's surface can be harnessed to enhance the cyclic stability of AFAs. Further research is needed to

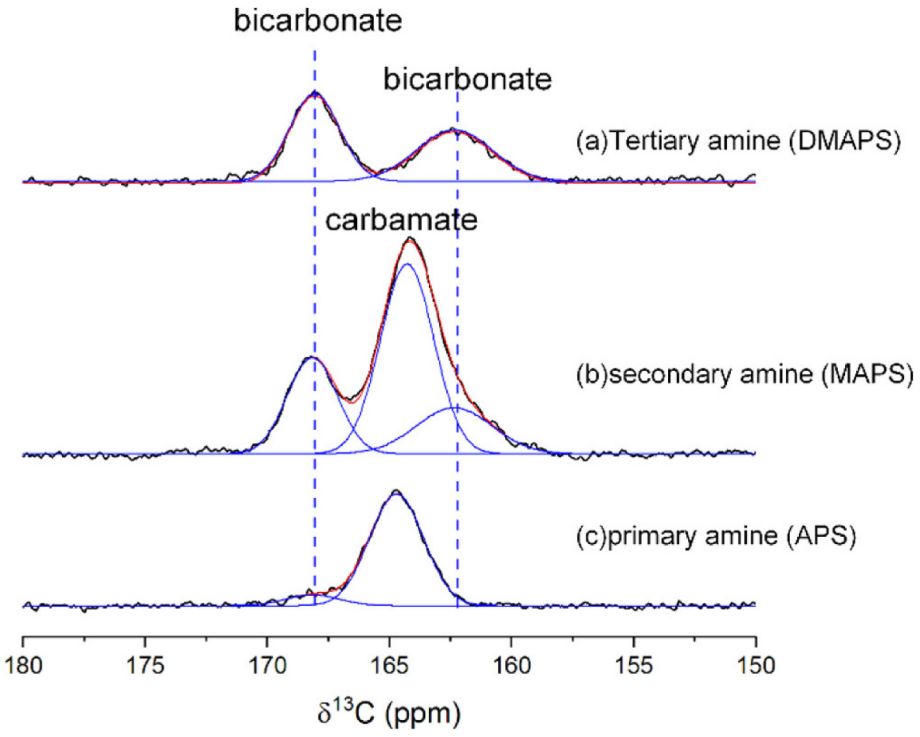

Fig. 38. ^{13}C CPMAS of H_2O-dampened $^{13}CO_2$-reacted (a) tertiary (DMAPS), (b) secondary (MAPS), and (c) primary (APS) amine pendant groups in SBA-15 recorded at 100 K [185].

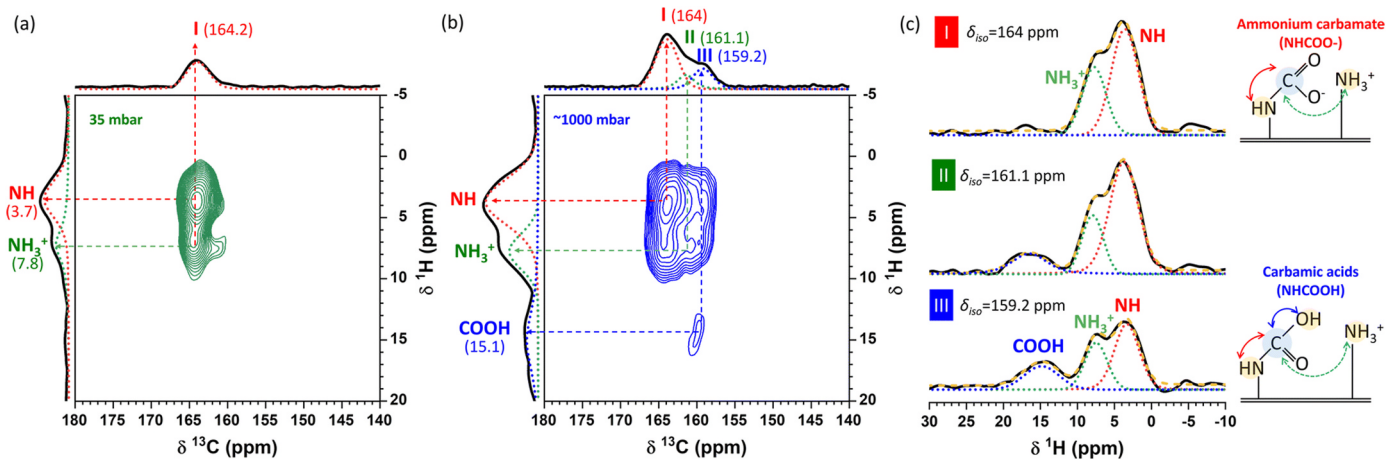

Fig. 39. Identification of the different chemisorbed species using 2D ^{1}H–^{13}C Heteronuclear Correlation (HETCOR) NMR.

address these complexities comprehensively and advance AFA materials for sustainable CO_2 capture applications. By bridging these knowledge gaps, future efforts can refine CO_2 capture technologies and contribute to mitigating climate change.

6. Conclusion

This study provides a current analysis of the factors impacting the thermal and cyclic stability of AFA, a key constraint limiting their broad industrial utilization. The review critically assesses ongoing efforts to improve the operational stability of AFA and identifies crucial areas requiring further research to advance the field. By unveiling the stability and host-guest interactions of amine-functionalized silica sorbents, this review propels the development and deployment of efficient and cost-effective carbon capture technologies. These carbon capture technologies play a crucial role in advancing several Sustainable Development Goals (SDGs), specifically Affordable and Clean Energy (SDG 7), Climate Action (SDG 13), and Industry, Innovation, and Infrastructure (SDG 9). By enabling effective capture and storage of CO_2 emissions, these technologies support the global transition towards net-zero emissions, thereby contributing to climate change mitigation. Consequently, based on the insights provided in the preceding sections, this study can be concluded as follows.

a. The exploration of thermal and cyclic stability mechanisms in AFA for CO_2 capture presents a multifaceted landscape of interrelated factors. Through extensive literature review, it is evident that AFA performance is intricately tied to various parameters, including amine and silica degradation, moisture sensitivity, support structure, chemisorbed species formation, and amine type and functionalization method.
b. The findings of this study underscore the complexity of thermal degradation in AFAs, challenging the simplistic attribution of failure solely to urea formation. Moisture's stabilizing effect beyond urea formation temperature calls for comprehensive investigations into its role in optimizing AFA performance.
c. Moreover, the wide range of factors impacting AFA stability emphasizes the importance of developing careful optimization strategies. Each aspect from the functionalization approach to the morphology of the support structure plays a vital role in achieving greater stability and adsorption capacity. Tailoring these parameters is critical for enhancing AFA resilience and efficiency under varying operational conditions.
d. Host-guest interactions within silica-based AFAs offer insights into CO_2 capture mechanisms, emphasizing the importance of managing amine density for efficient adsorption processes. While advancements have been made, knowledge gaps remain, particularly regarding diffusional limitations and the potential for leveraging host-guest dynamics to improve cyclic stability. Addressing these gaps will be key to further progress in AFA performance.
e. Finally, ongoing research efforts must focus on refining CO_2 capture technologies by addressing these complexities. By bridging knowledge gaps and optimizing AFA materials, we can advance sustainable CO_2 capture and contribute meaningfully to climate change mitigation. This necessitates collaborative endeavours across disciplines to drive innovation and propel CO_2 capture technologies towards practical implementation.

Despite the progress made in enhancing the thermal and cyclic stability of silica based AFAs, there remain unexplored areas that warrant additional research. These uncharted domains encompass the following.

a. Conduct research on the intricacies of CO_2 intraparticle-controlled mass transfer kinetics within amine-functionalized silica sorbents and the role of re-adsorption at amine sites in slow CO_2 uptake and desorption. This helps to understand mass transfer kinetics and identification of rate-limiting steps which will reveal the rate at which CO_2 molecules move into and out of the sorbent particles. Potentially, it may uncover whether the slow uptake or desorption of CO_2 is primarily governed by intraparticle diffusion, chemical reaction kinetics, or other factors. This information is crucial for optimizing CO_2 capture processes and designing efficient sorbent materials.
b. Examine the host-guest interactions within the AFA, encompassing the mechanisms governing adsorption, desorption, and the diffusion of CO_2 and impurities. Investigate how the structural characteristics of the support material influence these interactions. The study can help in selecting or designing adsorbents with tailored pore structures and surface functionalities for specific gas separation and purification applications.
c. Investigate the kinetics of CO_2 adsorption and desorption in AFAs, exploring the role of diffusion in these dynamic processes. It is important to delve into how impurities impact the diffusion of CO_2 within the adsorbent material. This study can aid researchers use the findings to develop models that accurately predict the performance of AFA under different operating conditions.
d. To gain a more profound comprehension of the structural modifications in amine-functionalized adsorbents (AFAs) over numerous operational cycles. Additionally, explore how differing moisture levels influence AFA performance, including the formation of bicarbonates and the potential for their reversibility. Investigating the formation of bicarbonates and their reversibility provides insights

into the long-term stability and regeneration potential of AFA. Researchers can assess the mechanisms involved in bicarbonate formation, identify factors influencing reversibility, and develop methods to enhance AFA regeneration efficiency.

e. Explore methods for enhancing the cyclic stability of AFAs by mitigating cross-linking. The study can elucidate the mechanisms and factors contributing to cross-linking in AFA and assist in understanding the challenges associated with cyclic stability. Insights from the study can inform the development of more efficient and cost-effective adsorption processes, contributing to the design and optimization of industrial-scale applications.
f. Study the factors contributing to diffusional limitations in AFAs and develop techniques to overcome these limitations, especially in the context of large-scale applications. This would improve on the economic viability of AFA.

CRediT authorship contribution statement

Briggs M.O. Ogunedo: Writing – original draft, Visualization, Funding acquisition, Conceptualization. **Basil Wadi:** Writing – review & editing. **Vasilije Manovic:** Visualization, Conceptualization. **Seyed Ali Nabavi:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

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

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Data availability

Data will be made available on request.

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