A review of N-functionalized solid adsorbents for post-combustion CO_2 capture

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Abstract

Over the past decade, amine-loaded solid adsorbents for capturing CO_2 from power plants have been widely studied. Various nitrogen (N) sources have been used for this purpose, and the current range of adsorbents, referred to here as N-functionalized solid adsorbent (NFSAs), are the subject of this review. The main synthesis methods of NFSAs are described and recent progress in the field discussed. Criteria for improving NFSA performance are highlighted with reference to a variety of solid supports, providing guidance on the selection of highly efficient, inexpensive adsorbents. A thorough assessment of adsorption mechanisms and factors influencing the adsorption process is given. The review concludes by exploring future research and development opportunities, as well as pathways for commercializing NFSAs.

Keywords: NFSAs; CO_2 capture; functionalization; amine; solid porous-based materials; adsorption performance

1. Introduction

About 40% of anthropogenic CO_2 emissions are produced by fossil fuel-based power plants. To meet the targets to maintain global temperatures within 2°C above pre-industrial levels by the end of the century, emissions need to significantly decrease [1, 2]. There are three approaches for capturing CO_2 from power plants: pre-combustion [3, 4], post-combustion [5-7], and oxy-fuel combustion [8, 9]. Post-combustion capture, which adsorbs CO_2 after fossil fuel combustion using wet/dry sorbents, is the most popular industrial method [10, 11].

To date, CO_2 absorption by aqueous amine of 20–30 wt % is still the state-of-the-art for post-combustion CO_2 capture processes, mainly due to the high CO_2 affinity of amines [12-14]. However, its application is restricted by several drawbacks, such as high equipment corrosion [7], intensive energy requirement for regeneration [12], tendency to degrade [15], and foaming issues [16]. Of the proposed alternative technologies for post-combustion CO_2 capture, adsorption-based technology is the most promising, due to its potentially lower cost while avoiding the drawbacks of aqueous amine. Adsorbents are the cornerstones for all adsorption processes, and numerous porous solid adsorbents have been developed for CO_2 adsorption in post-combustion gas conditions. However, these materials suffer either from low CO_2 affinity or low moisture toleration, and more importantly, are primarily used at low temperatures (under 30 °C) due to their rapid decline in capture capacity at higher temperatures [17-19].

N-functionalized solid adsorbents (NFSAs) are a group of adsorbents that have shown stronger CO_2 affinity than bare, porous adsorbents and have better moisture tolerance.

Therefore, NFSAs have been recognized as among the most promising post-combustion adsorbents for CO_2 adsorption from flue gas mixtures [20, 21]. NFSAs are produced by introducing electronegative N sources into solid adsorbents, taking advantage of both the pore structure of porous solid adsorbents and the acidic gas affinity of the N compounds. The electronegative nitrogen groups uniformly dispersed on the solid adsorbents provide abundant basic sites to adsorb acid gases, such as CO_2 and SO_2 [22].

Of the many published reviews on CO_2 capture, the majority mention amine-loaded materials as part of the discussion concerning solid adsorbents, reporting their properties and efficiencies for post-combustion CO_2 capture [7, 23, 24], or recommend them as efficient media for carbon capture and storage [25]. However, few papers summarize or compare different types of N-loaded adsorbents. For example, Darunte et al. [26] only investigated the progress of amine-loaded metal–organic frameworks (MOFs). Given the high potential of NFSAs as functionalized solid adsorbents for CO_2 capture, this paper presents a systematic, comprehensive review of these adsorbents to aid their further development. The review includes 1) NFSA synthesis methods and adsorption mechanisms; 2) approaches to improve adsorption capacity, thermal stability, and cyclic ability by investigating adsorbent supports; and 3) prospects for commercialization.

2. NFSA synthesis methods

The synthesis of NFSAs usually consists of two distinct steps: preparing solid supports, and combining N-source sorbents with the supports. Solid supports with high porosities and large pore volumes that are suitable candidates for N-loading include silica [27], zeolites [28], carbon-based materials [29], MOFs [30], polymers [31], and natural clay [32]. Except for natural clay, all these supports can be purchased or synthesized in the laboratory, and can therefore be developed into adsorbents by either loading and direct synthesis. Due to variations in the preparation process of support materials from case to case, especially when developing new supports, their synthesis methods are discussed in detail with the progress of NFSA in Section 3.

Regarding the loading of N sources on supports, synthetic methods of NFSA production have been classified into four approaches, based on the N sources used and the bonding styles between the N sources and the supports [33, 34]. The most commonly used N sources include monomeric (monoethanolamine [MEA], diethylamine [DEA] [35, 36]), oligomeric (diethylenetriamine [DETA] [15], tetraethylenepentamine [TEPA] [37], pentaethylenehexamine (PEHA) [38]), polymeric amine (linear and branch-polyetherimides, PEI [39, 40]), amino-containing ionic liquid [41], amino-containing pyridine, guanidine [42], alkoxysiliane [43], N_2, NH_3 and urea [29, 44]. The pros and cons of each NFSA synthesis method and their applications are summarized in Table 1 and described as following:

Impregnation (or wet impregnation) disperses amine species into porous supports. Typically, the selected amine is initially added into a solvent, usually water or organic solvents, such as methanol or ethanol. After dispersing the amine evenly by stirring, a certain amount of support is added into the amine solution continuously while stirring at room temperature for a certain time to help the amine molecules disperse into the pores of the support. The solution is filtered and dried to remove the solvent, and the amine-loaded adsorbent is then dried in an oven at 40 °C [37]. The amine molecules bonded on the surface and within the pores of the support form the adsorption sites for capturing CO_2. The loading of amine on the support substrate depends on the pore volume of the support. Functionalized adsorbents with higher adsorption capacities can be obtained from porous supports with large pore volumes. As there is no substantial chemical bond between the dispersed amines and the supports, the as-obtained adsorbents have similar thermal stabilities to the origins of the amines [35, 36].

Grafting covalently bonds amine-containing silanes or other grafted amines to solid supports. The amines are bound to the active (hydroxyl, etc.) groups of the substrate via silane chemistry or an analogous reaction mechanism. In contrast to impregnation, grafting usually includes a step to wash the unreacted amine molecules out of the sorbent using a solvent [45]. Hence, the number of active groups on the substrate surface is a crucial factor that determines the amine loading and adsorption performance [43]. The double functionalization method combining the above two methods has also been reported [46].

Ammoxidation is a unique method where the N source (N_2) attaches to the porous carbon materials by simultaneous oxidation and nitrogenation at a high temperature under aerobic conditions. The surface hydroxyl groups play an important role in anchoring nitrogen functionalities onto the carbon surface. Thus, the number of groups containing hydroxyl groups is an appropriate indicator to predict the adsorption performance of the N-doped adsorbents [47].

Direct synthesis produces N or amine-derived adsorbents with N-containing precursors by one-step, *in-situ* synthesis. Some synthetic materials (e.g. MOFs, polymers) with nitrogen-rich functionalities have been developed as solid adsorbents onto which N sources are attached. These materials have attracted further attention based on the development of simulation software that theoretically reveals the CO_2 capture mechanism [48, 49].

Two types of distinctive adsorbents have been synthesized using the above techniques: 1) adsorbents obtained by wet loading, such as impregnation and grafting, with the chemical adsorption as the dominant process; and 2) adsorbents prepared by N-doped methods, such as ammoxidation and direct synthesis, which mainly involve physical adsorption. These two types of adsorbents have different adsorption mechanisms, operation conditions, and applications. For convenience, this review classifies NFSAs into amine-loaded adsorbents and N-doped adsorbents based on their adsorption mechanisms.

Table 1 Summary of N-loading methods onto adsorbents and their characteristics

Method	**N source**	**Advantages**	
Impregnation	Monomeric or polymeric amine, amino acid, amino-containing ionic liquid, other amino-containing organic material except alkoxysilanes	● Higher amine loading than grafting ● Usually higher CO_2 adsorption capacity than grafting sorbents ● Repeatable synthesis method ● Mild synthesis conditions	● Weak connection material ● Weak thermal sta ● Surface amine ag
Grafting	Amine-containing alkoxysilanes	● Linkages between amino-material and substrate material are bonds ● Stable under a higher temperature (above 200 °C) ● Better amine dispersion degree ● Repeatable synthesis method ● Mild synthesis conditions	● Amine loadings group number ● Usually lower impregnation sorbe ● Lower channel ut ● Expensive amine
Ammoxidation	N_2	● Cheap N source ● Smaller effect on substrates ● High nitrogen content ● Good thermal stability	● Rigorous reaction
Direct synthesis	N-containing precursor	● One-step synthesis method ● Reported adsorbents usually have high adsorption performance	● No regular synthe

3. Amine-loaded adsorbents

The amine modification methods for all support materials are similar. Here, silica supports are taken as an example to illustrate the formation of amine-loaded adsorbents. Selected other supports are also described to complement the overall view of the studies.

3.1. Silica supports

Porous silica materials, such as MCM-41 and SBA-15, were the first porous solids used to develop NFSAs due to their high concentrations in surface silanol groups (Si-OH), ordered mesopore structures, and tunable pore sizes. Amines or amino-silanes were often loaded onto porous silica by wet impregnation or grafting methods. The promising adsorption capacities at moderate temperatures (40–80 °C) are consistent with the typical temperatures (45–55 °C) of the tail gases after decontamination, and the relatively low desorption temperatures compared with those of aqueous amine absorbents reduce the energy consumption of desorption [50]. These positive characteristics make porous silica materials the most widely researched for amine loading. The CO_2-adsorption performances of amino-silica and the corresponding functionalized materials are shown in Table 2.

Table 2. CO_2 adsorption performances of N-containing silica adsorbents

Silica	N source[a]	CO_2 adsorption capacity (mmol/g-sorbent)[b]			Adsorption conditions	Desorption conditions	Cyclic ability[c]	Ref.
		25°C	50°C	75°C				
MCM-41	–		0.33	0.20	100% CO_2			[27]
MCM-41	B-PEI, 50%	0.75		2.55	100% CO_2	100 °C, N_2	5.3%, 7	[51]
MCM-41	B-PEI, 50%			2.05	8% CO_2/N_2			[27]
Al-MCM-41-100	B-PEI, 50%			2.89	100% CO_2			[51]
MCM-41	PEI, 50%		2.51 (40)		15% CO_2/N_2	40 °C, N_2	64%, 3	[52]
MCM-41	MEA, 50%	0.91			100% CO_2			[53]
MCM-41	DEA, 50%	0.80			100% CO_2			[53]
MCM-41	TEA, 50%	0.94			100% CO_2			[53]
MCM-41	EDA, 40%	1.19 (30)			10% CO_2/N_2	100 °C, N_2		[34]
MCM-41	DETA, 40%	1.43 (30)			10% CO_2/N_2	100 °C, N_2		[34]
MCM-41	TEPA, 40%	1.96 (30)	2.25	3.51	10% CO_2/N_2	100 °C, N_2		[34]
MCM-41	PEHA, 40%	2.34 (30)	2.75	3.71	10% CO_2/N_2	100 °C, N_2		[34]
MCM-41	$[P_{4444}]$[2-Op], 5.0%		1.21		14.5% CO_2/N_2	120 °C, N_2		[54]
MCM-41	TEPA, 40%	2.70 (30)			10% CO_2/N_2	100 °C, N_2	7.4%, 10	[55]
MCM-41	PEI1800, 40%	1.30 (30)			10% CO_2/N_2	100 °C, N_2	0.01%, 10	[55]
MCM-41	APTS,30%, TEPA, 40%			3.50	15% CO_2/N_2	100 °C, N_2	4.32%, 15	[56]
PE-MCM-41	AP+TEPA, 50%		2.36 (45)		100% CO_2			[57]
MCM-41/silica gel,1:1	TEPA, 50%		4.27 (55)	342.6	15% CO_2/N	100 °C, N_2	6.6%,10	[58]
PE-MCM-41	DEA, 68.9%	2.36			5% CO_2/N_2	100 °C, N_2	3.3%, 7	[16]
AM	DETA, 60%			5.04	5% CO_2/He		8.5%, 6	[20]
EM	DETA, 60%			4.56	5% CO_2/He			[20]

MCM-41	PEI, 50%			7.92	100% CO_2	75 °C, N_2	14%, 120	[59]
MCM-41	TP, 9%			2.23	20% CO_2/N_2	75 °C, N_2	0%, 100	[60]
SBA-15	--		0.45 (45)		100% CO_2			[61]
SBA-15	B-PEI, 50%	0.83	1.71 (45)	2.04	100% CO_2	110 °C, Ar	3%, 10	[61]
SBA-15	TEPA, 50%		3.02 (45)		100% CO_2	110 °C, Ar	14%, 10	[61]
KIT-6	PEI, 50%			3.06	100% CO_2	75 °C, N_2	0%, 3	[62]
SBA-15	TEPA,30% DEA,20%			3.70	100% CO_2			[63]
SBA-15	PEHA, 50%			7.01(80)	12% CO_2/N_2	100 °C, N_2		[64]
SBA-15	DBU, 40%	1.37			15% CO_2+15% H_2O/N_2	80 °C, N_2	25.8%, 6	[65]
Silicic acid	AEEA, 55%	4.54			10% CO_2, 10% H_2O	90 °C, N_2	12%, 10	[66]
HMS	PEI, 50%		2.4 (45)		100% CO_2	110°C, --	0%, 4	[67]
MSU-F	TEPA,40% DEA,30%		5.91	5.03(70)	100% CO_2			[68]
MSU-F	TEPA,40% DEA,30%		5.53 (40)		20% CO_2/N_2			[68]
Silica monolith	PEI, 65%			4.77	100% CO_2			[69]
Silica monolith	TEPA, 65%			5.90	5% CO_2/N_2			[69]
MC400/10	TEPA, 83%			7.93	10% CO_2/N_2			[70]
FA	PEI			3.18	10% CO_2/N_2	100 °C, N_2		[71]

a The percentage of the N source represents the weight ratio of amine to adsorbent

b Adsorption temperatures other than 25, 50 and 75 °C are included in brackets

c The notation of cyclic ability marked is as "A%, B". A= the declining value of adsorption capacity, B= the total cycle number

3.1.1. Progress in amine-loaded silica adsorbents

For amine-loaded silica adsorbents, selection of suitable precursors and modification of the silica support itself are required to ensure the amino-solid adsorbents perform well. In terms of amine-screening, Song et al. [27] reported the introduction of branch-PEI into MCM-41 by wet impregnation. They observed that the CO_2 adsorption capacity increased from 8.6 mg CO_2/g-sorbent for the parent MCM-41 to 112 mg CO_2/g-sorbent (2.54 mmol/g-sorbent) for the functionalized adsorbent measured with pure CO_2 at 75 °C. They also found that the adsorption capacity of the modified MCM-41 was not significantly affected by the partial pressure of CO_2, with a value of 90.4 mg CO_2/g-sorbent at 8% of the CO_2 concentration. Ahmed et al. [53] investigated the adsorption capacities of MEA, DEA, and TEA (triethylamine)-impregnated MCM-41 to better understand the effect of amines on adsorbent performance. Under the same conditions, the adsorption capacities decreased in the order of MEA (primary), DEA (secondary), and TEA (tertiary amine). Liu et al. [34, 55] tested the effects of amine chain lengths and loading percentages of a series of amines (EDA [ethylene diamine], DETA, TEPA, PEHA) on the CO_2 adsorption performance of impregnated MCM-41. The adsorption capacities of short-chain, amine-based sorbents decreased with a rise in temperature, while the performances of long-chain, amine-based (TEPA, PEHA) sorbents showed a plateau after an initial increase and then decreased under the same conditions. This indicated that the CO_2 adsorption process is thermodynamically controlled for EDA and DETA-MCM-41, whereas for TEPA and PEHA-MCM41 it is kinetically controlled at low temperatures. Unlike long-chain, amine-based sorbents, short-chain amine-impregnated sorbents exhibit higher adsorption and desorption rates, mainly due less steric hindrance and lower diffusion resistance in the pores of the adsorbents. Lai et al. [66] developed a silicic acid adsorbent impregnated by a type of amine (aminoethylethanolamine [AEEA]) for CO_2 capture from flue gas. A maximum value of 4.54 mmol/g-sorbent reached for 55 wt% AEEA impregnated silicic acid compsite at 25°C under 10% CO_2 and 10% H_2O.

Hybrid-amine functionalization has been proven effective to improve the adsorption performance of silica. Wang et al. [46] developed hybrid-amine-loaded MCM-41 using APTS (3-aminopropyltrimeth-oxysilane) and TEPA via a two-step method of grafting followed by impregnation. An as-obtained sorbent with 30 wt% APTS and 40 wt% TEPA had the best adsorption capacity of 3.5 mmol/g-sorbent in 15% CO_2/N_2 gas mixture at 70 °C. This was much better than the optimal adsorption capacities of its single-amine-functionalized counterparts (MCM-41 with 60 wt% TEPA; 2.45 mmol/g-sorbent) under similar conditions. Sanz et al. [57] measured the adsorption capacity of different hybrid-amine-functionalized, pore-expanded MCM-41 using a similar method. Their results also suggested that hybrid functionalization is more useful to produce CO_2 adsorbents from PE-MCM-41 with higher performance than their grafted or impregnated counterparts. The synergistic effect of other N-containing materials, including ionic liquids to promote the adsorption capacity of MCM-41, were also studied [54, 72, 73].

Regarding the selection of supports, cost needs to be considered for large-scale applications. Selecting cheap materials to synthesize supports with proper quality is therefore beneficial. Bhagiyalakshmi et al. [74] and Qi et al. [75] chose rice husk ash and quartz sand, respectively, as silica sources to synthesize MCM-41, MCM-48, and

SBA-15 for amine loading. The highest adsorption capacities of 1.7 and 2.08 mmol/g-sorbent of CO_2 were reached on 3-CPA (3-chloropropyl amine hydrochloride)-grafted SBA-15 and AP-grafted MCM-41 at 25 °C, respectively. Wang et al. [76] prepared a type of PEI-loaded glass fiber with the maximal CO_2 adsorption capacity of 60.04 mg/g (1.36 mmol/g-sorbent) at a PEI/GF ratio of 0.7 g/g. Zhang et al. [71] invented a modified wet-impregnation method for preparing amine-impregnated silica from power-plant fly ash. By directly impregnating PEI into the wet support (pure CO_2-promoted sol-gel), the prepared sorbent could reach an adsorption capacity of 3.177 mmol/g-sorbent at 75 °C and 10 wt% CO_2/N_2, and even as high as 3.296 mmol/g-sorbent at 90 °C. The adsorption capacities of silica gels modified with DETA, TEPA and amine-containing silane were also measured, as silica gel is cheaper and more widely available than other silica-based supports [15, 77, 78].

Supports can be improved by modifying the support structure and porosity, followed by optimizing overall performance and minimizing production cost. Wang et al. [58] prepared a hierarchical MCM/silica gel support by physical mixing, and then impregnated it with TEPA for CO_2 adsorption. At 55 °C and 15 wt% CO_2/N_2, a maximum adsorption capacity of 4.27 mmol/g-sorbent was attained with 50% TEPA-loaded MCM/silica (1:1). This was due to the combination of mesoporous and microporous structures, which provided good CO_2 diffusion paths. By using silica gel as part of the raw materials, the production cost of the adsorbent is greatly reduced. The effect of the support's hierarchical pore structures in promoting CO_2 adsorption capacity was confirmed by Chen et al. [69] with a type of amine-impregnated, multi-scale, silica monolith.

Supports can be modified at any stage of the sorbent synthesis, as shown in Figure 1, using MCM-41 as an example [20, 59, 79] in which the factors in green boxes marked by stars could adjust the construction of MCM-41 to form the final sorbent products. The star-marked intermediates can also be employed as supports for amine loading.

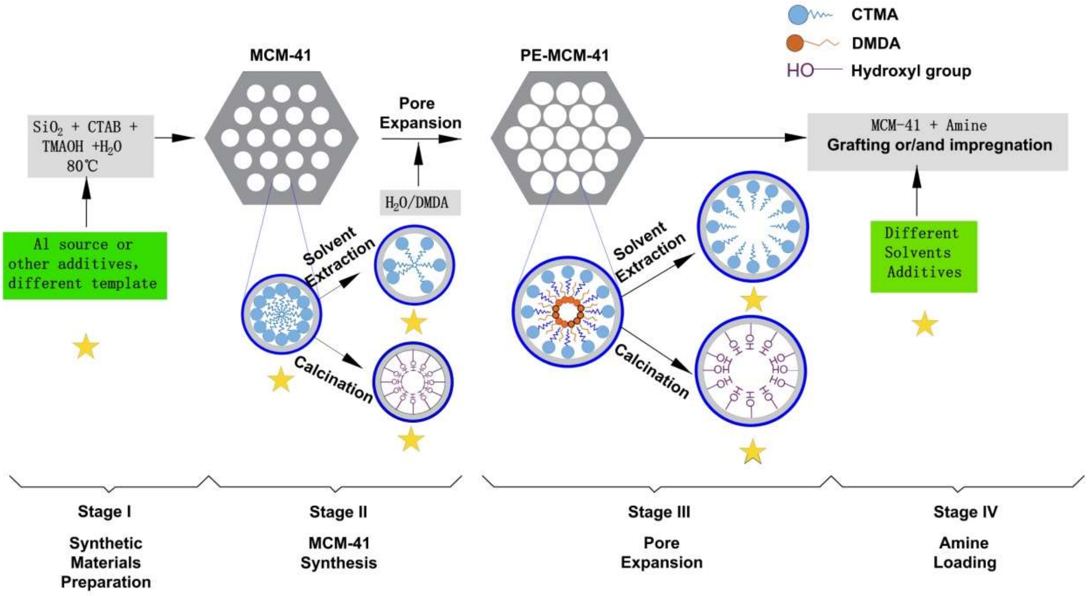


Figure 1. Modification process for adsorbent supports

At the first step of the synthesis of the porous adsorbent, marked as Stage I in the figure, a source of aluminum and other additives are added to the traditional compound to improve the performance of MCM-41 [27, 51]. The CO_2-adsorption capacities of MCM-22 and MCM-36 doped with different contents of Al or Fe also illustrated that the addition of metal atoms affects CO_2-adsorption capacity [80].

During the synthesis of MCM-41 and pore expansion stages (stages II and III in Figure 1, respectively), the products (occluded with template, extracted with solvents, calcined, pore-expanded MCM-41, and PE-MCM-4 extracted with solvents, etc.) are all suitable candidates for amine impregnation. Zhu's group [20, 33] investigated TEPA-modified MCM-41 following the same procedure and revealed the adsorption capacities of different 60% TEPA-impregnated MCM-41 adsorbents, with the ranks of pore-expanded (PM) > occluded with template (AM) > ethanol-extracted (EM) > calcined MCM-41(CM) in 5% CO_2/He at 75 °C. These results suggested that pore diameter plays an important role when choosing amine-impregnated supports, and the ordered template provides a spacious area for amine loading while restraining agglomeration. Son et al. [62] confirmed the conclusion that adsorbent performance was primarily influenced by their pore sizes by investigating CO_2 adsorption capacities of a series of 50 wt% PEI-impregnated silica supports – MCM-41 (pore diameter 2.8 nm), MCM-48 (3.1 nm), SBA-15 (5.5 nm), SBA-16 (4.1 nm), and KIT-6 (6.0 nm). Other researchers investigating the role of structural parameters of mesoporous silica also pointed out the importance of support pore sizes for amine-impregnated silica materials [81, 82]. The textural parameters of some popular solid supports are summarized in Table 3. Recently, Sanz-Pérez et al. [67] investigated the CO_2 adsorption capacities of PEI-impregnated HMS mesoporous silica materials (HMS) synthesized from amine-containing structure directing agents. The results suggested that remaining amines from non-removed amine-containing additives in the stage I have a synergistic effect on CO_2 capture with impregnated amines.

As for amine-grafted adsorbents, according to the investigations of Wang et al. [83] on CO_2-adsorption capacity of amine-grafted sorbents with different surface silanol densities, the variations between the SBA materials treated with different processes were mainly caused by the differences of silane content on the support surfaces.

Table 3. Textural parameters of solid supports for N-loading

Solid supports	Surface area (BET) (m^2/g)	Pore volume (cm^3/g)	Pore diameter (BJH) (nm)	Ref.
Silica materials				
MCM-41	1490	0.99	3.3	[22]
PE-MCM-41[a]	1230	3.09	11.7	[22]
MCM-48	1162	1.17	3.1	[36]
MCM-22	481	0.40	18.2	[84]
MCM-36	575	0.70	18	[84]
SBA-15(C)[b]	725	1.12	9.3	[33]
SBA-15(P)[b]	345	0.71	8.9	[33]
SBA-15(CP)[b]	100	0.2	7.1	[33]
PE-SBA-15 [a]	428	1.18	15.2	[85]
SBA-16	736	0.75	4.1	[62]
KIT-6	895	1.22	6.0	[62]
MSU-H	744	1.43		[86]
MSU-F silica	600	2.41	22.4	[87]
HMS mesoporous silica	1181	0.96	2.1	[67]
Amorphous silica gel	567	0.67	36.8	[88]
Commercial silica gel	604	0.52	2.0	[15]
Hexagonal mesoporous silica	909	1.06	29.6	[88]
Monodispersed porous silica microspheres	921	0.48	2.1	[89]
Silica-aerogel	822	5.	42	[77]
Periodic mesoporous organosilicas	759	0.92	6.1	[90]

Mesocellular silica foam	532	1.82	11.3	[81]
Carbon-based materials				
Activated carbon (palm shell)	882	0.03		[91]
Commercial activated carbon	545	0.48	3.5	[92]
Activated carbon (delayed coke)	889	0.49	5.7	[93]
Mesoporous carbon	757	3.61	29	[94]
MWCNTs [c]	120	0.42	9.7	[95]
Metal–organic frameworks				
CAU-1	1268	1.32		[21]
Mg_2(dobpdc)	894			[96]
ZIF-8	1150			[97]
Polymers				
OC 1065 IER (Lanxess)	26	0.26	15.4	[98]
PGMA[d]	121		60.2	[99]
Poly divinylbenzene	789	0.97		[100]
MBMOP[e]	1082	4.13	0.5	[101]
Zeolites				
13X	615	0.34	1.1	[102]
5A	334	0.18		[103]
ZSM-5	705	0.66		[104]
β-zeolite	574	0.23	6.5	[105]
Metallic compounds				
Titanate nanotube	303	0.96	11.1	[106]

Titanate nanotube	341	1.20	14.9	[41]
Titanate nanotube (T3)	306	1.07	10.2	[107]
Porous $MgCO_3$	280	0.18	3.9	[108]
Natural clay minerals				
Kaolinite	74			[109]
Sepiolite	220	0.60		[110]
Acid Sepiolite	272	1.07		[110]
Hydrotalcite	165	0.57	124.9	[111]
Laponite	358		27.5	[112]

a PE = pore-expanded

b SBA-15(P), SBA-15(C), SBA-15(CP) refer to water-washed SBA-15 without calcination, calcined SBA-15 at 550°C to remove the template, and SBA-15 prepared by impregnation P123 into SBA-15(C), respectively, as described in the reference

c MWCNTs = multi-walled carbon nanotubes

d PGMA = poly(glycidyl methacrylate)

e MBMOP = melamine-based microporous organic polymer

In the amine-loading stage (Stage IV in Figure 1), the solvent applied has a great impact on the performance of MCM-41. Zhao et al. [79] chose AEAPDMS (N-β-(aminoethyl)-γ-aminopropyldimethoxy methylsilane) to modify MCM-41 in different solvents to test their influences on the adsorbents using the grafting method. Polar solvent tetrahydrofuran (THF) and nonpolar solvent toluene were selected, as they can promote the CO_2-adsorption ability of grafted MCM-41. The highest adsorption capacity of 2.20 mmol/g-sorbent on amine-loaded MCM-41 was obtained in toluene at 70 °C. Zhang et al. [113] prepared PEI-loaded silica gel using different additives, which increased the accessibility of the adsorption sites and further improved the gel's CO_2 adsorption ability.

3.1.2. Adsorption mechanism

Typical CO_2 adsorption–desorption isotherms of MCM and its amine derivatives are shown in Figure 2. There are two distinctive behaviors in these experimental isotherms. The isotherm of the original MCM-41 showed that CO_2 adsorption capacity is low at low pressure, but increases almost linearly as the pressure rises, and has a completely reversible desorption process due to its physical adsorption mechanism. In contrast, the amine-loaded silica showed higher CO_2-adsorption capacity at lower pressure and less dependency on pressure at higher pressure, as well as an irreversible adsorption–desorption process according to its chemisorption-like mechanism [52]. Furthermore, the hysteresis between the desorption and adsorption branches of these isotherms increases with the amine content. A horizontal, or slightly upward trend is also noticed in the desorption branch of the high amine-loaded silica due to the kinetic restrictions to CO_2 desorption from these materials [43, 57, 114]. An average adsorption enthalpy of 60 kJ/mol was calculated (larger than ~22 kJ/mol, the typical value for physical adsorption between silica support and CO_2) [99, 115].

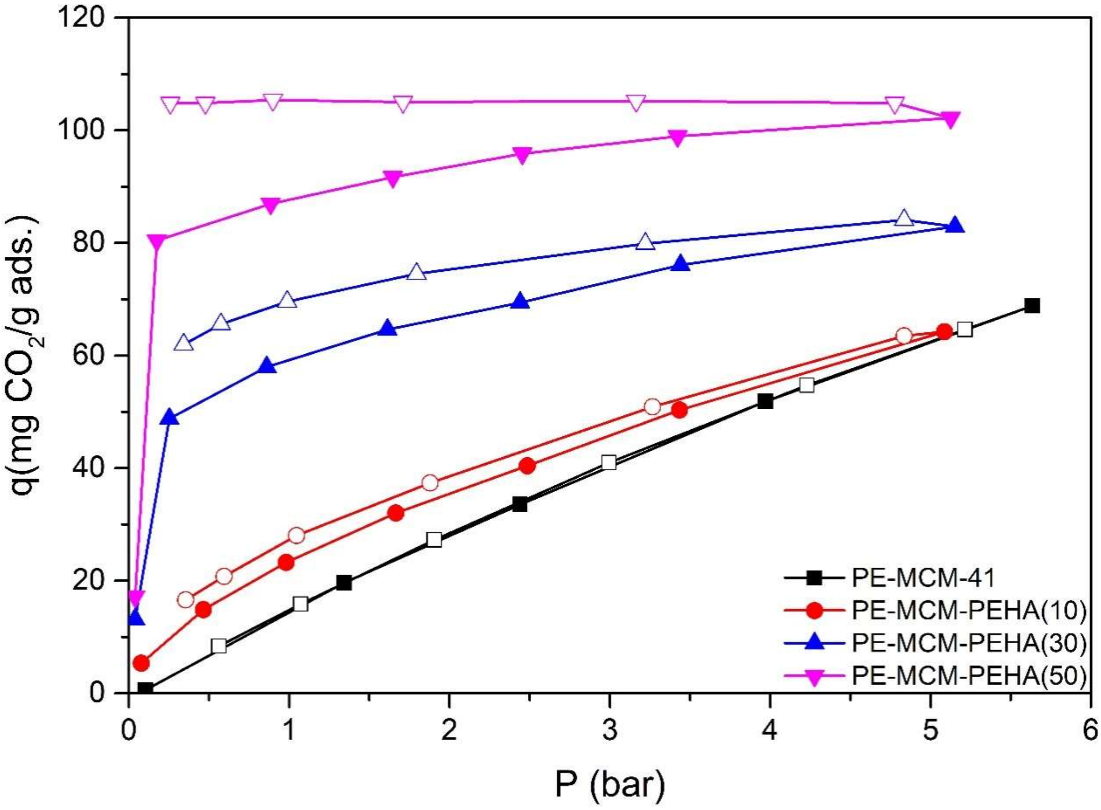


Figure 2. The CO_2 adsorption–desorption isotherms of silica and its amine derivatives (solid points: adsorption process, hollow points: desorption process) [57]

The bonding types between amines and supports differ from the amine-loaded methods. In wet impregnation, the amine disperses into the pore channels of the supports, stretches out on the inner pore surface, fills the pores gradually, and finally covers the outer surface with increasing amine loading. The amines bond with the support and with each other through hydrogen bonds [40]. In the grafting technique, amine groups are anchored on the surface of the silica, forming chemical bonds using silane coupling agents [43]. The linkage types between the different amino-silanes and the support are shown in Figure 3 [42, 116]. These bonds reinforce the stability of adsorbents while limiting the maximum amine loading on the support. In turn, this leads to a lower CO_2 adsorption capacity of amine-grafted adsorbent compared with the impregnated adsorbent [117]. However, the inadequate but relatively uniform amine grafting provides a sterically favored structure for further amine impregnation to produce more efficient adsorbents [46].

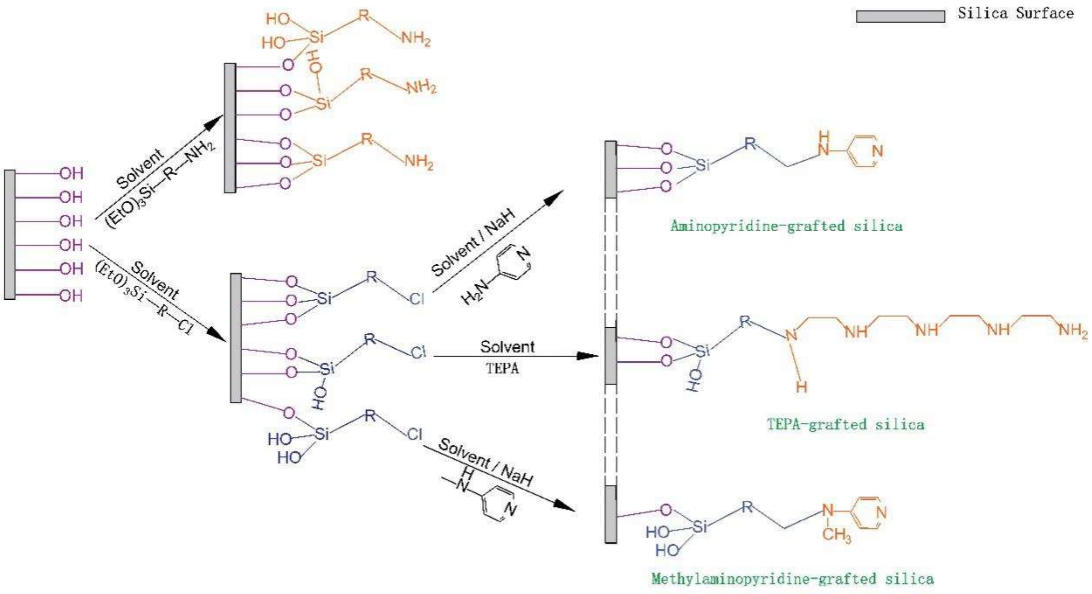


Figure 3. Amine grafting scheme on mesoporous silica [42, 116]; R- represents an aliphatic carbon chain with or without additional secondary amine

Surface area, pore volume, and other textural properties of the silica that determine the physical adsorption capacity of the functionalized material decrease as the pores are filled by amines. This become more obvious with longer organosilane chains in grafted materials, and with higher loadings of the molecules in the impregnated supports. Hence, in amine-loaded silica, where the surface area of the silica is decreased, the adsorption process is most likely dominated by chemisorption rather than physical adsorption [61]. The interaction between the basic amino sites and the acidic CO_2 molecules follows the zwitterion mechanism described by Caplow [118].

For primary and secondary amines, the involved mechanisms are described via equations 1–5:

$$CO_2 + RNH_2 \leftrightarrow RNH_2^+COO^- \qquad (1)$$

$$RNH_2^+COO^- + RNH_2 \leftrightarrow RNHCOO^- + RNH_3^+ \qquad (2)$$

$$RNH_2^+COO^- + R_1R_2NH \leftrightarrow RNHCOO^- + R_1R_2NH_2^+ \qquad (3)$$

$$CO_2 + R_1R_2NH \leftrightarrow R_1R_2NH^+COO^- \qquad (4)$$

$$R_1R_2NH^+COO^- + R_1R_2NH \leftrightarrow R_1R_2NCOO^- + R_1R_2NH_2^+ \qquad (5)$$

where R, R_1 and R_2 represent different aliphatic carbon chains or hydrogen. The lone pair of electrons on the amine R_1R_2NH attacks CO_2 to form the CO_2-amine zwitterions. Another free R_1R_2N deprotonates the zwitterion and forms the carbamate salt of carbamic acid and ammonium. These reactions occur between amine intra or inter-molecules with the same (equations 1, 2 or 4, 5) or different (equations 1, 3) types of amines [34, 53, 117]. Each molecule of CO_2 can bond to two nearby amines to form ammonium carbamate species in an anhydrous CO_2 flow.

An *in-situ* Fourier-transform infrared (IR) spectroscopy study before and after CO_2 adsorption illustrated the CO_2 adsorption over the amine-loaded silica sorbent (Wang et al [117]). The study confirmed the formation of alkylammonium carbamate species after CO_2 adsorption. The variation of the IR band intensities with time of CO_2 adsorption rates at different temperatures suggests the presence of two adsorption rate regimes. The first is rapid adsorption of CO_2 onto the exposed amine groups located on the outer surface of multilayered amines inside the pore channels, which is controlled by the adsorption affinity or thermodynamics. The second is the slower diffusion of CO_2 molecules from the surface into the bulk of the multilayered amines to access more amine groups, which is controlled by the diffusion, depending on the spatial flexibility of the polymer chains packed inside the mesopores. Using similar techniques, Zhai et al. [119] demonstrated that the formation of ammonium carbamates related to -NH_2 groups is faster than the formation of carbamic acid structures originating from the interaction between -NH and CO_2. The latter is slower in the adsorption process, but easier in the desorption process.

The molar ratio of reacted CO_2 and amine equals 1:1 when water is introduced. The mechanisms are described via equations 6–11:

$$RNHCOO^- + CO_2 + 2H_2O \leftrightarrow RNH_3 \cdot HCO_3 + HCO_3^- \quad (6)$$

$$HCO_3^- + RNH_3^+ \leftrightarrow \quad RNH_3 \cdot HCO_3 \quad (7)$$

$$R_1R_2NCOO^- + CO_2 + 2H_2O \leftrightarrow R_1R_2NH_2 \cdot HCO_3 + HCO_3^- \quad (8)$$

$$HCO_3^- + R_1R_2NH_2^+ \leftrightarrow R_1R_2NH_2 \cdot HCO_3 \quad (9)$$

$$RNH_2 + CO_2 + H_2O \leftrightarrow RNH_3 \cdot HCO_3 \quad (10)$$

$$R_1R_2NH + CO_2 + H_2O \leftrightarrow R_1R_2NH_2 \cdot HCO_3 \quad (11)$$

Under this condition, CO_2 is removed through the formation of bicarbonate [120, 121]. For tertiary amines, the reaction proceeds only when water is present. The mechanism involves the base-catalyzed hydration of CO_2 with H_2O associated with the reaction of CO_2 with tertiary amines, as described in equations 12–14 [122]:

$$R_1R_2R_3N + H_2O \leftrightarrow R_1R_2R_3NH^+ + OH^- \quad (12)$$

$$OH^- + CO_2 \leftrightarrow HCO_3^- \quad (13)$$

$$HCO_3^- + R_1R_2R_3NH^+ \leftrightarrow R_1R_2R_3NH \cdot HCO_3 \tag{14}$$

Amine efficiency (AE), defined as the moles of captured CO_2 divided by the moles of N (CO_2/N ratio) per mass unit, is one of the most popularly referred indicators to reflect adsorbent efficiency [39, 57, 99]. Theoretically, the AEs of the interaction between CO_2 and amine are 0.5 and 1 under dry and humid conditions, respectively. It would be expected that the overall AEs of the adsorbents should be slightly higher when additional physical adsorption takes place on the support. However, the actual value is usually lower than the theoretical value, as demonstrated in Figure 4. There are two possible reasons that can explain this phenomenon. First, the formation of hydrogen bonds between the adjacent amine groups, or between amines and the support, inactivates the amines and prevents them from adsorbing CO_2 [121]. The second possibility is due to the inaccessibility of the active sites for CO_2 molecules, as the multilayered amines generate diffusion limitation in highly loaded sorbents [60]. Thus, it is understandable that the adsorbents with moderate amine loadings – normally those obtained from grafting having lower amine loadings and more ordered amine distribution, or obtained from a combined grafting-impregnation method with ordered amine distribution – usually have larger CO_2/N ratios [56, 123].

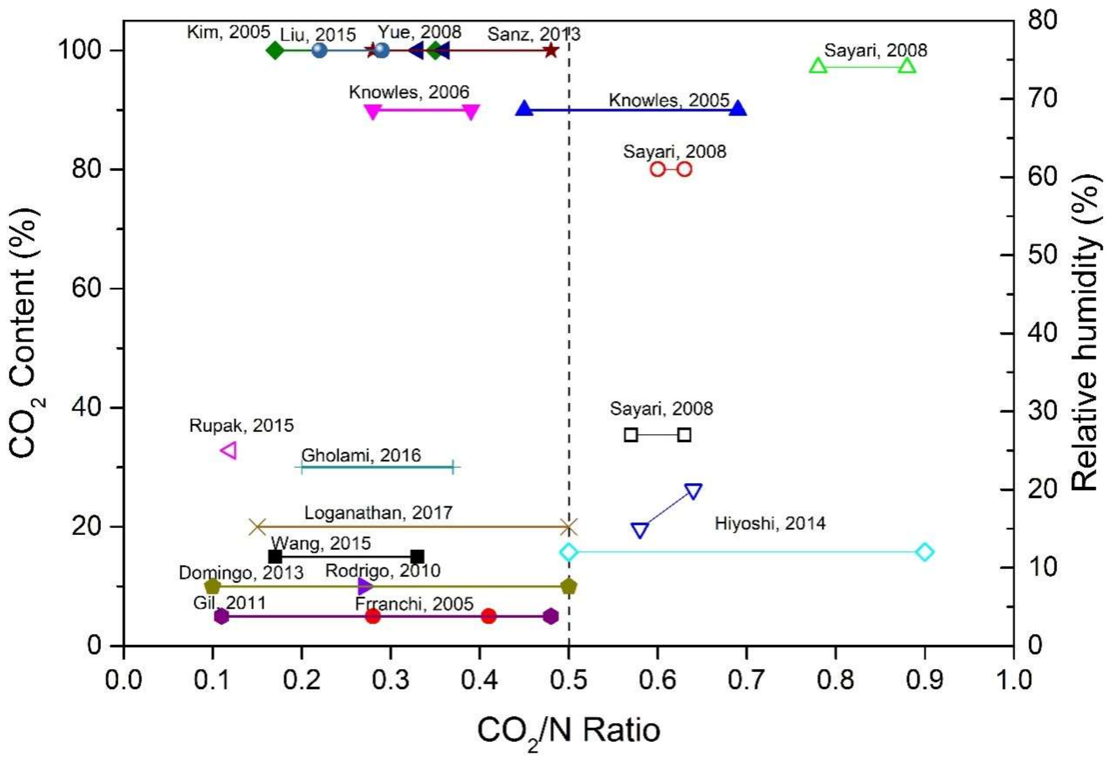


Figure 4. CO_2/N ratios of amine-loaded adsorbents under different simulated flue gases (solid point, with different CO_2 concentrations (%) under dry condition; hollow point, under different wet conditions)

3.1.3. Thermal stability, durability and cyclic ability

Thermal stability

Thermal stability is a critical parameter of amine-loaded silica. The decomposition temperature of sorbents can directly affect the selection of temperatures for CO_2 desorption and sorbent regeneration in a temperature swing adsorption (TSA) process, both at the laboratory level and on a large scale [74]. The thermostability of mesoporous silica is much high than that of amines. Figure 5, extracted from Liu et al's study [55], shows the thermogravimetric analysis curves of MCM-41 and its amine-loaded (40 wt% based on sorbent) derivatives. The weight loss of MCM-41 is negligible when most of the loaded amine evaporates under elevated temperatures;

consequently, the thermal stability of amine-loaded silica is affected by the amines it contains. As shown in the TEPA-MCM-41 curve, there is a rapid decrease before 100 °C, which can be attributed to the desorption of CO_2 and the moisture. Amines begin to decompose at higher temperatures with a sharp weight loss at 135 °C and at 231 °C. The total weight loss of EDA, TEPA, PEI-600 and PEI-1800 loaded MCM-41 at this region is 9.2, 33, 35.4, and 38.1 wt%, respectively (Figure 5). The differences between the experimental and the theoretical (40 wt%) values suggest that some of the amine might volatilize together with the solvent during preparation; therefore, more of the large-molecular-weight amines with higher boiling points were loaded on the silica.

The structures and related properties of commonly used amines are listed in Table 4. Generally, there are two decomposition processes: the evaporation of amine molecules weakly adhered to the outside surface of the silica or to other amines, and the decomposition of amine molecules anchored to the inner face of the silica [35]. Even though the specific association between the boiling point and the decomposition temperature is ambiguous, the variation in decomposition temperatures is in accordance with the changes in the boiling points for the same type of amines. The decomposition temperatures among amines with similar amine amounts follows the order of hydramines > amine-containing silanes > polyamines. Although not accurate, the boiling point is still an important indicator of the thermostability of amine-loaded silica.

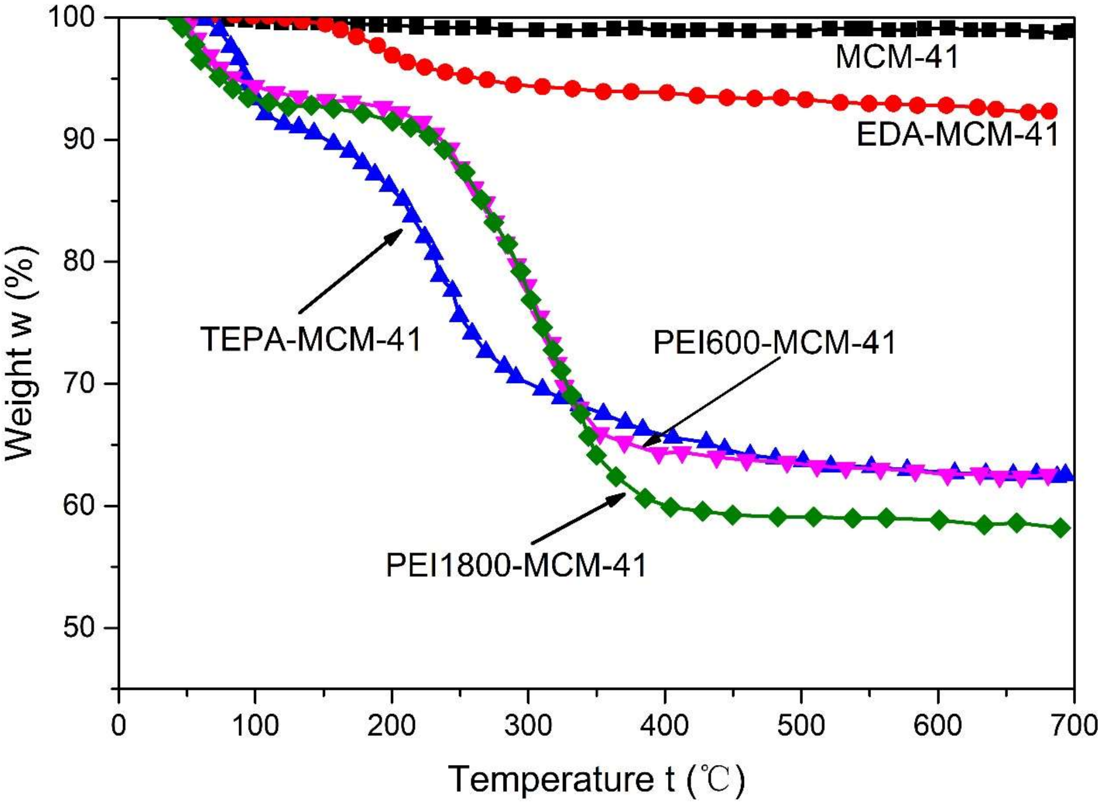
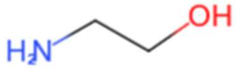
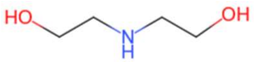
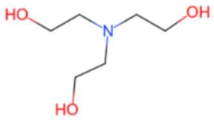
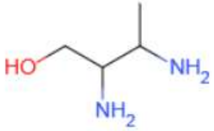
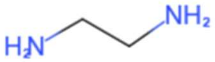
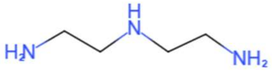
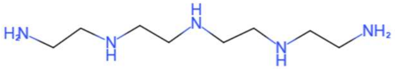
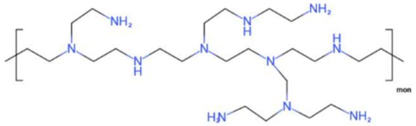
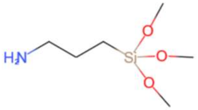
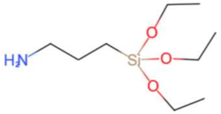
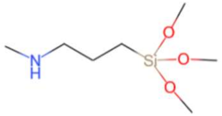


Figure 5. Thermogravimetric analysis curves of mesoporous MCM-41 silica material and its amine-loaded derivatives [55]

Table 4. The structure and physical properties of amines

Amine/abbreviation	Structure	BP/WLT/°C[a]
Ethanolamine/ ETA/MEA		170/300, 400 [35]
Diethanolamine/ DEA		268.8/300, 450 [35]
Triethanolamine/ TEA		360/273,501 [89]
Aminoethylethanolamine/AEEA		-/110, 180[66]
1,2-ethylenediamine/ EDA		116/102 (177) [34]
Diethylenetriamine/ DETA		207/130(235) [15]
Triethylenetetramine/ TETA		278/110 (150) [124]

Tetraethylene-pentamine/ TEPA		340.3/135 (231) [125]
Pentaethylene-hexamine/PEHA		380/151 (240) [34]
Polyethylenimide/PEI		205/125, 217 [27, 126], 310 [55]
3-aminopropyl trimethoxysilane/APTMS		194/125, 277 [126]
3-aminopropyl triethoxysilane/APTES		217/ 147 (267) [127]
[3-(methylamino)propyl] trimethoxysilane/MAPS		–/200 (290) [128]

a BP = boiling point, WLT=weight loss temperature when loaded on supports.

Notation marked as A/B, C: A=boiling point, B= evaporation temperature, C=rapid decomposition temperature.

Notation marked as A/B (C): A=boiling point, B= initial decomposition temperature, C =sharp decomposition temperature.

Durability

The durability of adsorbents is composed of their cyclic ability and storage time. Good cyclic performances usually indicate low energy consumption. Three main techniques used to evaluate the cyclic abilities of adsorbents are TSA, vacuum swing adsorption (VSA), and pressure swing adsorption (PSA), in which increase in temperature, evacuation, and flushing with an inert gas are employed to desorb CO_2, respectively. Combinations of these techniques, such as TSA+PSA and TSA+VSA, are often adopted to improve desorption efficiency. From the cyclic abilities of adsorbents listed in Table 2, it can be seen that the cyclic performance of amine-loaded silica is highly stable under appropriate conditions. The cyclic stability highly depends on the thermal stability of the loaded amine and the type of the bonds between the N and the support. Liu et al. [55] tested the cyclic ability of different amine-loaded MCM-41 adsorbents prepared with same impregnation method, and found stability to be in the order of TEPA< PEI600< PEI11800, while the cyclic ability shrank from 7.4 to 0.01%. Loganathan et al. [60] evaluated the cyclic ability of amine-grafted adsorbents, 3-aminopropyl triethoxy silane (AP) and N-(3-trimethoxysilylpropyl) diethylenetriamine (TP)-loaded PE-MCM-41, and found that the change in the adsorption capacity up to 100 cycles was almost negligible.

Generally, the reduction of adsorption capacity for amine-loaded silica reflected by the cyclic curves in pure CO_2 may be due to the following reasons:

- **Incomplete desorption of CO_2.** A low desorption temperature leads to incomplete desorption of CO_2, which causes a sharp decrease in the adsorption capacity after a certain number of cycles [52].

- **Amine loss.** Amine loss is the main reason for permanent loss of adsorption capacities. For short-chain, amine-loaded adsorbents, spontaneous evaporation of amine at low temperatures is responsible for the loss. As a result, they usually have weaker cyclic abilities than their long-chain, amine-loaded counterparts. Selecting a high desorption temperature can also accelerate amine loss for amine-loaded silica adsorbents. Continuous heating, cooling, and stabilization at a moderate temperature can also result in a faster amine loss [55].

- **Amine conversion.** Sayari et al. [59] investigated the stability of PEI-loaded MCM-41 by testing both adsorption and desorption at 75° C by PSA through 120 adsorption–desorption cycles. They observed a 14% weight loss after 120 cycles, partly due to the formation of urea at the expense of amine groups under dry conditions, while water vapor can inhibit this reaction via the formation of bicarbonate (equation 10). The possible reaction mechanism of the formation of urea is shown in equation 15 [129]:

$$2RNH_2 + CO_2 \leftrightarrow (RNH)_2CO \ \ (Urea, stable) + H_2O \tag{15}$$

This mechanism also suggests that selectively using secondary amines rather than primary amines can inhibit amine conversion.

Kishor et al. [81] investigated how the long-term stability of amine-loaded silica related to storage time. Even after 6 months, the adsorption capacity of PEHA-loaded KIT-6 was undiminished.

Recycling ability

Recycling adsorbents after reaching their lifespan can reduce the cost of preparation. Sanz-pérez et al. [130] investigated recycling amine-grafted and impregnated SBA-15 by calcination and subsequent re-functionalization with amine. Adsorbents originally prepared by impregnation maintained their CO_2 adsorption properties even after 6 cycles, while the CO_2 adsorption capacities of those originally prepared via grafting reduced progressively due to the loss of silanol groups on the surface.

3.1.4. Effect of the support structure

Preparing porous silica with hierarchical structures and organic–inorganic hybrid materials are two ways to obtain new superior supports.

In the first approach, Qi et al. [70, 131] synthesized hollow, spherical particles with mesoporous shells, denoted as mesoporous silica capsules (MC), with different sizes and shell thicknesses. By using polystyrene (PS) latex as the template for the formation of hollow interiors and cetyltrimethylammonium bromide (CTAB) as the mesoporous template, the tuned mesoporous silica was impregnated with PEI or TEPA to make CO_2 adsorbents. Benefiting from the hierarchical structure of MCs, which provided a hollow space for larger amine loadings, and a mesoporous shell, which provided tunnels for CO_2 diffusion, the as-prepared sorbents exhibited a maximum adsorption capacity of 7.93 mmol/g-sorbent using simulated flue gas at 75 °C and retained more than 90% of their CO_2-adsorbing capacity after 50 cycles.

Liu et al. [103] fabricated a mesoporous silica shell and used it to cover commercial 5A microporous zeolite pellets. Macromolecular PEI was then successfully impregnated into the silica shell, while the 5A zeolite pellets were unaffected, due to their smaller pore size compared to the size of the PEI molecules. Amine can both increase the CO_2 adsorption capacity of the sorbent, and hinder the diffusion of water molecules into the zeolite core to maintain good CO_2-adsorption capacity under humid flue gas conditions. The as-synthesized adsorbent with 30 wt% PEI loading had an outstanding adsorption capacity of 5.05 mmol/g-sorbent in the simulated humid flue gas at 25 °C, and a good cyclic stability after 10 adsorption–desorption operations.

Ko et al. [132] fabricated double-walled, silica nanotubes (DWSNT) using a tubular compound, 2-amino-N-dodecylacetamide (ADAA), as the template through the co-condensation method. CO_2-adsorption capacities of various aminosilane-loaded DWSNT (primary, secondary, tertiary, di-, and tri-loaded) were tested in a TSA process at various adsorption temperatures under pure CO_2 or simulated gas mixtures. The adsorption capacities were in the order of tri- > di- > primary > secondary > tertiary amines and were consistent with the conclusion reached in Section 3.1.1.

For the second approach, Canck et al. [90] synthesized a type of hybrid, periodic, mesoporous organosilica material (PMOs). In a typical process, a polysilane (commonly a bis-silane $(R'O)_3$–Si–R–Si–$(OR')_3$) that contains an organic bridge (R) is coated on the template by co-condensation. After removal of the template, a highly porous material with organic hydrophobic bridges is prepared. A wide range of diamines and polyamines are grafted in the PMOs through a two-step method combining bromination of the double bond in the PMO and substitution with NH^2-R-NH^2 to improve CO_2-adsorption capacity. From the perspective of AE, diaminododecane (DADD)-grafted PMO was considered as a proper candidate for CO_2 chemisorption under dry conditions. A similarly ordered mesoporous organosilica (OMO) with cyanopropyl groups was obtained by co-condensation with a template made of Pluronic P123 triblock copolymer under acidic conditions by Gunathilake et al. [133] Hydroxylamine hydrochloride (Hy)-grafted OMO by means of ammoxidation was used to adsorb CO_2. At 60 °C, 60% amidoxime-loaded OMO (CP-40%-AO) reached a maximum CO_2-sorption capacity of 3.28 mmol/g-sorbent under an atmosphere of pure CO_2.

3.1.5. Effect of gas impurities

In industrial applications, the flue gases from post-combustion power plants usually contain 11–15% CO_2, 70–80% N_2, 5–12% H_2O, 3–6% O_2, 200–4000 ppm SO_2, 200–800 ppm NO_2, and other trace impurities[134]. The impurities affect the adsorption capacities of adsorbents via different routes.

Nitrogen is usually adsorbed through physical interaction with the adsorbent. As a result, the adsorption capacity of nitrogen decreases sharply to a negligible level as adsorption temperature rises. In contrast, moderate heating can promote the chemisorption of CO_2 and consequently, the selectivity measured by the molar ratio of CO_2/N_2 can be larger. However, the change in selectivity based on pressure changes is unknown. According to a theoretical simulation by Zhu et al. [135] for 60 amine groups grafted to MCM-41, the selectivity of CO_2/N_2 decreased from ~1000 to 280 when the pressure increased from 0 to 100 kPa. However, Belmabkhout et al. [22] observed an opposite trend when they measured CO_2/N_2 selectivity in MCM-41, pore-expanded MCM-41, and amine-loaded MCM-41 from 0 to 2 MPa at 25 °C. They found that selectivity dramatically increased from 9 to 308 for amine-modified MCM-41, due to the great affinity between the amine and the acid gas at 25 °C. Despite these differences, probably originating from the variation in amines or amine loadings, the selectivity ratio was sufficiently high under all tested conditions, possibly due to the nature of amine-loaded silica. As mentioned above, surface area and pore volume decrease rapidly when amine is loaded, which might be the main reason for the decrease in physical adsorption. In addition, CO_2 molecules occupy most amine sites due to their affinity, further weakening nitrogen adsorption. Therefore, nitrogen can be treated as inert gas in most cases. Amine-loaded silica adsorbents also do not adsorb CO[43, 61, 136].

O_2 is usually inert at low temperature. However, amine oxidation proceeded via free radical formation by the reaction of O_2 with amines at elevated temperatures can causes rapid deactivation for amine-loaded silica adsorbents. Ahmadalinezhad et al. investigated the oxidative degradation of amine-grafted [137] and amine-impregnated [138] adsorbents caused by amine oxidation by NMR techniques. The results showed the generation of structural units containing –C=O and –CH=N– species in both cases. For PEI-impregnated adsorbents, the linear PEI is more stable than the branched PEI after O_2 exposure for 24h at elevated temperatures (80 – 120 °C). Recently, Min et al. [139] developed a PEI-impregnated silica adsorbent with high oxidative stability by functionalizing PEI with 1,2-epoxybutane and pre-supporting chelators onto silica supports. The former strategy generates tethered 2-hydroxybutyl groups, which inhibits amine oxidation. The latter strategy poisons p.p.m-level metal impurities that catalyse amine oxidation. The resultant adsorbent showed a loss of adsorption capacity of 8.5% after 30 days aging in O_2-containign gas at 110 °C.

In industrial applications, the dehydration process (especially for removing trace amounts of moisture before flue gas treatment) can significantly increase operating costs. Hence, tolerance to moisture becomes an important indicator to assess whether an adsorbent is suitable for industrial use. As part of the reaction leading to bicarbonate formation on amine-modified silica via reactions 6–11, water promotes CO_2 adsorption and inhibits urea formation, thus increasing cyclic ability [140] (see also Section 3.1.2). Zhang et al. [65] synthesized 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)-modified SBA-15, and evaluated the promoting effect of water for CO_2 adsorption from simulated flue gas. When the volume ratio of CO_2 and H_2O was 1:1, SBA-15-(DBU-X) had optimum CO_2 adsorption capacity, consistent with the reaction mechanism described with equation 10. Zhang et al. [39] investigated the effect of water at different temperatures and various humidity levels. Adsorbents containing similar loadings of branched and linear PEI molecules were prepared and treated under 10% CO_2 from 0 to 17.2 mg/g of specific humidity (SH) at 25–55 °C. The best adsorption capacity was observed when adsorbents were exposed to an SH=11.5 mg H_2O/g at 25 °C. Further increasing SH did not show additional benefit for linear PEI, and even decreased CO_2 uptake for branched PEI. At higher temperatures, the difference in adsorption capacity between dry and humid conditions decreased, mainly due to the much lower water adsorption capabilities at the higher temperatures. However, silica pores may collapse after steam treatment for a long period of time. Min et al. [141] developed a PEI-impregnated silica with thick framework (> 10nm) to overcome this drawback. The adsorbents showed greater stability due to suppressed Ostwald ripening of framework after 14 days steam treatment at 120°C. Hammache et al. [142] investigated the impact of steam on a PEI-impregnated silica adsorbent using multiple steam cycles at 105 °C. The results reveal that steam can cause the decrease of adsorption capacity due to the reagglomeration of the amine in the pores rather than the collapse of pores.

NO_2, a type of acidic gas naturally affinitive to amine, is adsorbed simultaneously with CO_2. However, its products, formed via chemisorption, are too stable to desorb at the operation temperatures of amine-loaded sorbents. This reduces adsorption capacities and reduces the operational life of the sorbents [136]. The presence of SO_2 causes the same issues, as shown by Sanz-Péreze et al. [61], who evaluated the influence of SO_2 on CO_2 adsorption performance in continuous adsorption–desorption cycles under a 1000-ppm SO_2-containing stream. The SO_2–NH_2 reaction produces sulfate and bisulfite, like the CO_2–NH_2 reaction. During the second and successive cycles, the adsorption capacities fell steeply, due to the irreversibility of the SO_2–NH_2 reaction under the regeneration conditions (110°C under the flow of nitrogen) as a result of the strong bonds formed between SO_2 and amino-groups. Recently, Kim et al. [143] developed a SO_2-resistant PEI-impregnated silica for CO_2 adsorption by using the fact that SO_2 adsorption onto tertiary amines is fully reversible. By selectively converting the impregnated PEI to tertiary amines with epoxide, the resultant adsorbent showed an 8.52% loss of adsorption capacity after 1000 adsorption-desorption cycles in the presence of 50 ppm SO_2.

3.2. Other materials

In addition to silica, solids such as zeolites, carbon-based materials, MOFs, polymers, metallic compounds, and natural clay are possible supports for amine loading. These supports, especially for mesoporous materials, usually possess similar properties to amine-loaded silica [144-146]. However, due to differences in surface properties and porous structures, these supports may exhibit different adsorption mechanisms and stabilities, which will be the focus of this section. The adsorption capacities and regeneration abilities of these adsorbents are summarized in Table 5.

Table 5. CO_2-adsorption performances of amine-loaded adsorbents

Support materials	N source[a]	CO_2-adsorption capacity (mmol/g-sorbent)[b]			Adsorption conditions	Desorption conditions	Cyclic ability[c]	Ref.
		25 °C	50 °C	75 °C				
Chitosan	TETA	13.65			CO_2, 4 MPa			[92]
Activated carbon	TETA	16.16			CO_2, 4 MPa			[92]
Activated carbon	DEA		5.65		66% CO_2/N_2	110°C, N_2	14%, 15	[93]
Mesoporous carbon	PEI		4.84 (65)		15% CO_2/N_2	100°C, N_2	4%,10	[94]
N-activated carbon	TEPA		3.38 (60)		15% CO_2/N_2	100°C, N_2	5.6%, 10	[147]
Meso-activated carbon	TETA			1.85	10% CO_2/He	75°C, He	9%, 4	[148]
C_{60}	PEI			3.20	100% CO_2	90°C, Ar	40%, 100	[144]
Multi-walled CNT	TEPA		2.75 (60)	3.09 (70)	CO_2, trace SO_2	150°C, N_2	20%, 5	[149]
KOH-MWCNT	TEPA		5 (60)		10% CO_2/N_2, 1% H_2O	90°C, N_2	16%, 10	[150]
CNT	LPEI			1.89 (70)	100% CO_2	110°C, N_2	0%, 7	[151]
CNT	B-PEI			2.43 (70)	100% CO_2	110°C, N_2	14.66%, 7	[151]
CNT	APTS	1.93			15% CO_2, wet	150°C, N_2	28%, 100	[152]
Y60	TEPA		2.56 (60)		15% CO_2/N_2	75°C, N_2	10%, 9	[50]
Y60	TEPA		4.32 (60)		15% CO_2, wet			[50]
NaY	[APMIM]Br	4.94 (0)			100% CO_2	50°C, N_2	5%, 20	[153]
β-zeolite	APTES	4.71 (35)			100% CO_2	60°C, N_2	0%, 9	[145]
ZSM-5	EDA			6.13	100% CO_2, wet			[104]
Mg-MOF-74	TEPA	5.682			100% CO_2			[30]
Mg/DOBDC	EDA	1.50			400 ppm/Ar	120°C, Ar	0%, 4	[154]
UiO-66	PEI			2.41	CO_2, 55% RH	120°C, N_2		[146]
ZIF-8	PEI		1.61 (65)		50% CO_2/N_2			[97]

ZIF-8	PEI		1.99 (65)		50% CO_2/N_2, 55% RH			[97]
PGMA	PEI hydrogel		4.85		80% RH, CO_2	110 °C, N_2	0%, 8	[99]
PDVB	VI, 70%	2.35			100% CO_2		0%, 7	[100]
PDVB	VT,70%	2.65			100% CO_2		0%, 7	[100]
PDVB	PEI, 58%	3.60	3.25	3.76	100% CO_2	75 °C, N_2	0%, 10	[155]
PDVB	PEI, 58%	3.10	3.50	3.25	15% CO_2/N_2	75 °C, N_2	0%, 10	[155]
LDH (MgAl DS)	DAEAPT	0.70	1.10 (60)	1.76 (80)	100% CO_2			[156]
TiO_2 nanotube	MEA	1.07 (30)			15% CO_2/N_2			[106]
TiO_2 nanotube	EDA	1.09 (30)			15% CO_2/N_2			[106]
TiO_2 nanotube	TETA	2.70 (30)			15% CO_2/N_2			[106]
TiO_2 nanotube	PEI	2.55 (30)			15% CO_2/N_2			[157]
TiO_2 nanotube	TEPA	4.10 (30)			15% CO_2/N_2	100 °C, N_2	5%, 10	[106]
Protoned TiNT	TETA			4.33	10% CO_2/N_2	75 °C, N_2	9.9%, 6	[107]
Protoned TiNT	TETA			4.83	10% CO_2, wet			[107]
Porous $MgCO_3$	PEI, 20%			1.07	100% CO_2	100 °C, N_2	7.5%, 10	[108]
Kaolinite	MEA+EDA			3.39	100% CO_2	100 °C, N_2		[109]
Acid sepiolite	DETA	1.65 (35)			100% CO_2	75 °C, N_2	4.8%, 4	[110]
Hydrotalcite	TEPA			6.1 (80)	30% CO_2/He	130 °C, He	4.92%, 8	[111]
Montmorillonite	AEAPTS/CTAB			1.80 (100)	15% CO_2/N_2	160 °C/N_2	0%, 9	[32]
Montmorillonite	AEAPTS/CTAB			1.15 (100)	15% CO_2/SO_2	160 °C/N_2	83%, 9	[32]

a The percentage after the N source represents the weight ratio of amine to adsorbent
b Adsorption temperatures other than 25°C, 50°C and 75°C are included in the brackets
c The notation marked as A%, B: A = declining value of adsorption capacity, B = total cycle number

3.2.1. Amine-loaded, carbon-based materials

Carbon-based materials vary from the cheap, widely used activated carbon (AC) to the state-of-the-art carbon nanotube (CNT), and can all be used for gas adsorption and separation due to their immense surface areas (Table 3). Amine-loaded mesoporous carbons [144], carbon nanotubes [149, 158], and some ACs [147] all show similar properties to amine-loaded silica adsorbents due to their mesoporous nature.

Some new techniques were introduced to obtain these adsorbents. AC supports are usually prepared from lignocelluloses, such as palm shell, oil sands coke, or different ranks of coals as precursors, via acid or alkaline treatment and high-temperature N_2-activation steps to improve their textural properties. Amine loading helps improve their CO_2 adsorption capability [91-93]. Gholidoust et al. [93, 115] found that DEA-loaded AC from oil sand coke, activated with KOH, had a maximum adsorption capacity of 5.65 mmol/g-sorbent at 50 °C, which is 75% higher than the commercial 13X zeolite. Similarly, using KOH as an activation agent to increase the surface area and porosity of multi-walled CNT, Irani et al. [150] made a TEPA-loaded CNT that reached an adsorption of 5 mmol/g-sorbent for a gas mixture containing 10% CO_2/N_2 with 1% H_2O at 60 °C.

The controllable pore size of AC also provides a platform to study the effect of pore size on the adsorption capacity of the obtained adsorbent. Gibson et al. [148] impregnated microporous and mesoporous AC with EDA and TETA and confirmed that microporous materials are inappropriate for amine impregnation, as the filling of the outer pores causes pore blockage. This inhibits further penetration of amines into the internal pore space.

More recently, studies have focused on practical issues. Zhou et al. [151] compared the CO_2 adsorption performance of L-and B-PEI-loaded CNTs. The CO_2 adsorption on L-PEI (1.89 mmol/g-sorbent) was lower than that on B-PEI-coated CNT (2.43 mmol/g-sorbent). However, lower desorption temperature and better stability after steam treatment made the L-PEI-CNT more suitable for a longer period of CO_2 adsorption. To overcome the brittle nature of the amine-functionalized carbon nanotubes (NCs), which may cause problems such as clogged pipes or recycling issues, Iqbal et al. [159] modified NCs with carbon nanofibers (CNFs) by electrospinning followed by carbonization. This significantly increased CO_2 adsorption and improved the NCs' strength, porosity, and flexibility. The modified adsorbents (NC@CNFs) achieved a CO_2 uptake of 6.3 mmol/g-sorbent at 25 °C and 100 kPa, and also had good CO_2/N_2 selectivity and cyclability. The synthesis procedure of the sorbents and improvements in properties are shown in Figure 6.

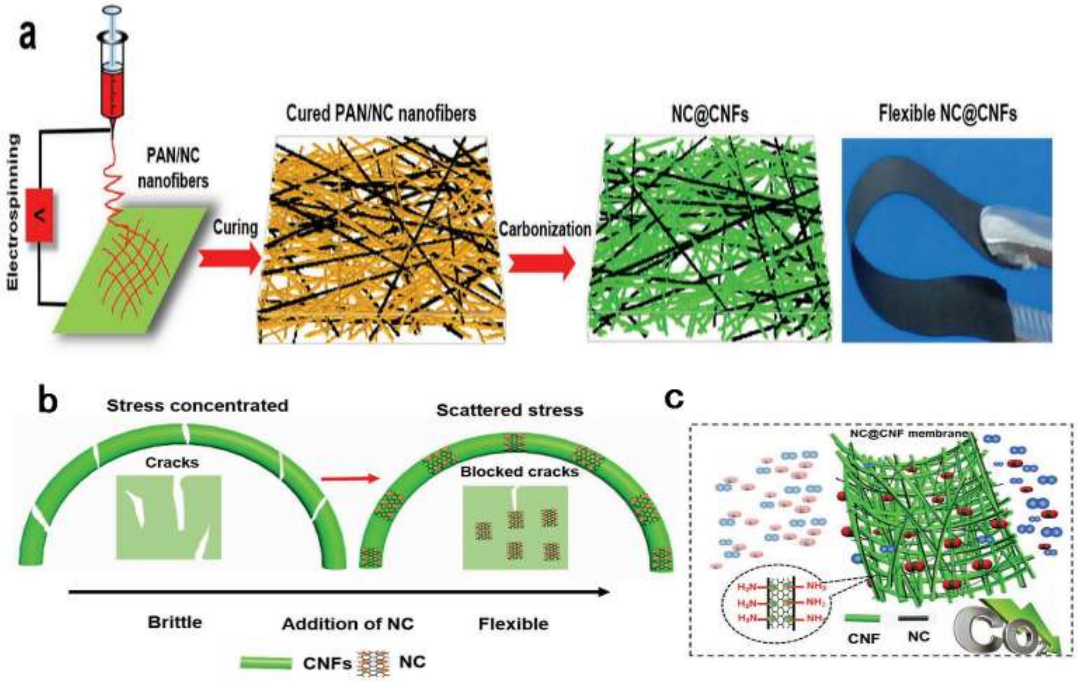


Figure 6. a. Synthesis pathway of NC@CNFs, b. schematic illustration of the structure and plausible mechanism of mechanical flexibility, and c. CO_2 capture from flue gases using the flexible nature of NC@CNFs [159]

Su et al. [152] assembled an APTS-grafted CNT into a dual-column temperature–vacuum swing adsorption (TVSA) system to evaluate the multi-cycle stabilities of loaded sorbents for CO_2 adsorption under dry and wet gas streams. After 100 TVSA cycles, the CO_2 adsorption capacity of CNT(APTS) was notably increased in the presence of saturated water vapor at 25 °C. To assess the effect of scale on amino-loaded carbon adsorbents, Gibson et al. [160] developed a series of adsorption columns from a few milligrams up to 1 kilogram of adsorbents using zero length column, extended zero length column, dual piston PSA, and self-developed rotary wheel adsorbers, respectively. These columns, along with the relevant methods, were used for initial rapid screening of adsorbents for CO_2 adsorption at low partial pressures, to obtain reliable adsorption parameters at different scales for model validation and adsorption performance prediction.

3.2.2. Amine-loaded zeolites

Zeolites are some of the most widely used gas separation microporous materials [161, 162]. Hundreds of different zeolites, such as A-, X-, and ZSM-5 types, have now been synthesized in the laboratory for different separation tasks. Some mesoporous zeolites have also been prepared [145, 163]. The uniform frame structure of zeolites takes the shape of a network of interconnecting channels or cages for adsorbing or capturing gas molecules [164]. The large surface area and the existence of metal cations, such as Li, Na, and Al, improve the polarity of zeolites, making them suitable for CO_2 capture [165-168]. In addition, the CO_2-adsorption performance of their amine-loaded derivatives is close to that of amine-loaded silica.

Due to the physical adsorption nature of microporous zeolite adsorbents and their rapid decrease in capture capacity with temperature, they are mainly used at low temperature. Their adsorption performance also decreases under humid conditions [169]. Amine loading can partly overcome these problems; however, the small pore size of microporous zeolites hinders amine loading and CO_2 diffusion into pores. Small molecular monoamines, oligomeric amines, amine-containing silanes, and hydramines can impregnate the micropores of pristine zeolites, but the boiling points of these amines are relatively low, while the required dehydration temperature of zeolites is usually as high as 350 °C. Residual moisture can affect the accuracy of adsorption capacity measurements [102, 105]. Nonetheless, amine-loaded zeolites are still studied by many groups, as they are much cheaper than mesoporous silica. The adsorption capacity and CO_2 selectivity over nitrogen of amine-loaded zeolites at high temperatures were improved in a similar manner as their microporous carbon material analogs due to the chemisorption sites provided by amines, even though in some cases adsorption capacities decreased compared to the original support materials [102, 170]. Su et al. [50] loaded commercially available Y-type zeolite with TEPA (Y60 [TEPA]) and demonstrated that 60 °C (rather than 25 °C) was the optimal temperature for CO_2 adsorption, because of the appropriate chemical interaction and van der Waals forces between CO_2 molecules and the surface of Y60 (TEPA). The adsorption capacity of Y60 (TEPA) at 15% CO_2/N_2 reached 112.7 and 189.9 mg/g (2.561 and 4.316 mmol/g-sorbent) under dry and moisture (optimal humidity 7%) conditions, respectively. Ninety percent of the adsorption capacity was maintained after 20 cycles at dry atmosphere, reflecting the adsorbent's good cyclic ability.

For mesoporous zeolites, some new techniques and applications have been studied to make the adsorbents more efficient. Kalantarifard et al.[104] synthesized EDA impregnated ZSM-5 for CO_2 adsorption, with the highest CO_2 adsorption capacity obtained being 6.13 mmol/g-sorbent in the presence of water at 75 °C. Microwave heating was employed for the desorption process, and the fastest desorption time was 9 min for 70% EDA loaded ZSM-5. To further reduce the cost of adsorbents, Thakkar et al. [171] prepared ZSM-5, zeolite-Y(ZY) and SAPO-34 from kaolin clay and modified them with TEPA for capturing CO_2 from air. The best adsorption capacity was 1.12 mmol/g-sorbent for the TEPA-loaded ZY at 25 °C using 5000 ppm CO_2 in nitrogen.

Some strategies for improving amine-loading techniques based on the unique cage structures of microporous zeolites have also been employed. Yu et al. [153] prepared NaY zeolites loaded with amine-functionalized ionic liquids using the innovative ship-in-a-bottle method. Based on the unique large-cage–small-pore structure of NaY zeolite, an *in-situ* synthesis method was employed to directly assemble a large molecular ionic liquid (MIL), 1-aminopropyl-3-methylimidazolium bromide ([APMIM]Br), in an NaY super cage that is larger than the pore size of NaY. The overall capture capacity was 4.94 mmol/g-sorbent, and the chemically adsorbed CO_2 was 1.85 mmol/g-sorbent at 0°C with pure CO_2. The lower desorption temperature (50 °C, N_2) and good cyclic ability (5% of decrease for the adsorption capacity after 20 adsorption–desorption cycles) shows great potential for future industrial CO_2 capturing.

3.2.3. Amine-loaded MOFs

MOFs and other materials with similar structures, such as zeolite imidazole framework (ZIF) and zeolitic tetrazolate framework (ZTF), are promising novel adsorbents for CO_2 capture due to their high surface areas, large pore volumes, and easy tunable compositions and pore structures [172]. Amine loading can tremendously improve the water tolerances of MOFs. Xian et al.[146] synthesized PEI-impregnated UiO-66 (PEI@UiO-66) for CO_2 capture. The CO_2 adsorption capacity of PEI@UiO-66 at 65 °C reached 1.65 and 2.41 mmol/g-sorbent under dry and wet conditions, respectively. Multiple consecutive adsorption–regeneration tests suggested that the CO_2 working capacity of PEI@UiO-66 can be fully recovered after cyclic regeneration. Su et al. [30] investigated the adsorption capacity of TEPA-modified Mg-MOF-74 and its wet stability. The adsorption capacity of amino-Mg-MOF-74 (TEPA-MOF) for CO_2 was as high as 26.9 wt% of the sorbents (~5.682 mmol/g-sorbent) at 25 °C. The wet stability of the MOF structure improved under humid conditions, as the amine layer protects the MOF structure against H_2O entry, as shown in Figure 7. ZIF, a subclass of metal–organic framework, has attracted many attentions for CO_2 adsorption, due to its zeolitic-like structure with a metal–imidazole–metal angle of 145° and good water resistance. Xian et al. [97] impregnated PEI into ZIF-8 for CO_2/N_2 separation and investigated the effect of water on CO_2 adsorption. The adsorption capacity and CO_2/N_2 selectivity of the PEI-modified ZIF-8 (PEI@ZIF-8) in 50% CO_2/N_2 mixture at 65 °C reached 1.61 mmol/g-sorbent and selectivity of 62 under dry conditions, and 1.99 mmol/g-sorbent and selectivity of 89.3 at 55% relative humidity (RH). This was due to the synergetic action of water and PEI. To illustrate the effect of MOF supports on the adsorption capacity of amino-impregnated MOF materials, Martinez et al. [173] prepared HKUST-1, MIL-53(Al) and ZIF-8 modified with TEPA for CO_2 capture under post-combustion conditions (75% N_2, 5% O_2, 14% CO_2, 6% H_2O, 45°C, 100 kPa). ZIF-8 had a better distribution of TEPA due to the lack of reactive surface sites compared to its analogs HKUST-1 (unsaturated copper sites) and MIL 53(Al) (exposed hydroxyl bridges (μ_2-OH)). Therefore, the modified adsorbent possessed a better adsorption capacity under both dry and wet conditions.

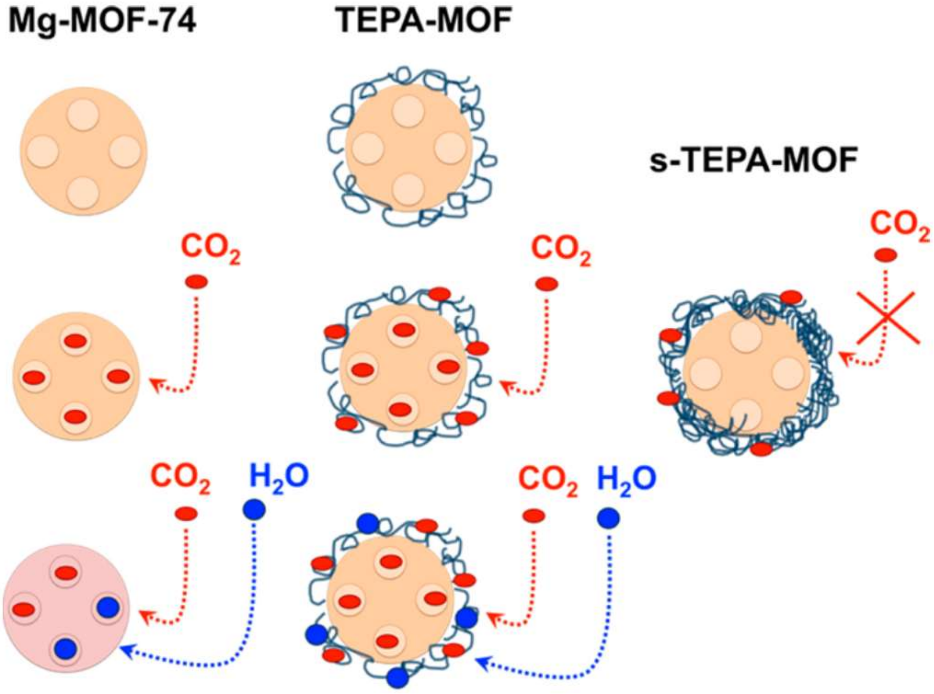


Figure 7. Schematic diagram of the effect of tetraethylenepentamine (TEPA) on metal–organic frameworks (MOF). Mg-MOF allows H_2O and CO_2 to enter, but H_2O damages the crystal structure (first column). An amine layer formed by a moderate amount of TEPA protects the MOF against H_2O entry, while allowing CO_2 (second column). Saturation of the particle prevents both CO_2 and H_2O from entering and thus reduces adsorption capacity (third column). Reprinted with permission from Su et al. [30]. Copyright(2017) American Chemical Society.

3.2.4. Amine-loaded polymers

For amine-loaded polymers, researchers have focused on amine selection and polymer preparation. Jiang et al. [174] synthesized a series of amino acid (AA) and AA-complex-loaded, porous polymethylmethacrylate (PMMA) sorbents for CO_2 capture. A mixture of arginine–polystyrene sulfonate improved the adsorption capacity of PMMA up to 1.3 mmol/g-sorbent at 25 °C. To directly increase the adsorption of CO_2 from humid flue gases, Han et al. [99] impregnated PEI hydrogel onto the inner face of poly(glycidyl methacrylate) (PGMA) porous materials using 1, 4-butanediol diacrylate (BDA) as the cross-linker. The 25 wt% PEI hydrogel-impregnated PGMA with a BDA/PEI ratio of 0.25 had the highest adsorption capacity of 4.85 mmol/g-sorbent at 40 °C and RH of 80%. It also had a selectivity of 37.9 over nitrogen, due to the effective take-up of moisture into this material and the CO_2 affinity of the amine sites.

Mesoporous polydivinylbenzene (PDVB) materials have been synthesized using different techniques and loaded with amines for CO_2 adsorption. Jafari et al. [100] synthesized mesoporous PDVB materials using 2, 2'-Azobis(2-methylpropionitrile) (AIBN) as the initiator through microwave-assisted polymerization and then impregnated the material with the amine-rich co-monomers of vinylimidazole (VI) and vinyl triazole (VT). By having more active sites, VT-modified PDVB had a maximum CO_2 adsorption of 2.65 mmol/g-sorbent at 0 °C under 100 kPa, while the adsorption capacity of VI-modified PDVB was 2.35 mmol/g-sorbent under the same conditions. Liu et al.[155] prepared PDVB through one-pot, timsolvothermal polymerization and impregnated them with PEI. The optimum formulation was 58 wt% PEI (to the adsorbent) impregnated PDVB (0.58PEI@PDVB) with maximum adsorption capacities of 3.76 and 3.00 mmol/g-sorbent under pure CO_2 and 10% CO_2, respectively, at 75 °C. The stability under both conditions was maintained after 10 adsorption cycles in both dry and wet conditions.

3.2.5. Amine-loaded metallic compounds

Porous metallic compounds are usually used as adsorbents or supports for CO_2 capturing under intermediate (200–400 °C) and high (>400 °C) temperatures through chemisorption [175]. However, some research has also been conducted at low adsorption temperatures for amine-loaded materials. Wang et al. [156] investigated the adsorption capacities of doubly layered hydroxides (LDH, Mg Al DS) grafted by 3-[2-(2-Aminoethylamino) ethylamino]propyl-trimethoxysilane (DAEAPTS) at different temperatures. A maximum adsorption of 1.76 mmol/g-sorbent was achieved at 80 °C due to the influence of primary and secondary amines in the sorbents. Song et al. [106, 157] screened the effect of different amines (PEI, MEA, EDA, TETA, TEPA) to promote the CO_2 adsorption capacity of Ti-nanotube (TiNT) material. The adsorption capacity increased in the order of MEA, EDA, PEI, TETA, and TEPA-loaded TiNT. TiNT-TEPA-69 showed the highest adsorption capacity of approximately 4.10 mmol/g-sorbent at 30 °C, and only dropped by 5% after 10 adsorption–desorption cycles. Guo et al. [107] investigated the CO_2 adsorption capacity of amine-impregnated protonated titanate nanotubes (PTNT). The highest CO_2 sorption capacity was 4.33 mmol/g-sorbent for the PTNT with 60 wt% TETA loading under 10% CO_2 in nitrogen at 75 °C. Yuan et al. [41] synthesized amine-containing ionic liquid (imidazolium-based poly(ionic liquid)) brushes to modify titanate nanotubes using the grafting technique. The achieved CO_2 adsorption capacity of the synthesized poly(ionic liquid) brushes with a polymer content of 46 wt% was 2.43 mmol/g-sorbent at 25 °C under a CO_2 partial pressure of 20 kPa. Temperature-programmed desorption profiles revealed that the adsorption of CO_2 on the β-carbon of imidazole rings is physical, while the interaction of CO_2 with amine groups is chemisorption. More recently, Wan et al.[108] investigated the CO_2 adsorption performances of a PEI-impregnated porous $MgCO_3$ that obtained by using MgO and CO_2 as the raw materials. 20% PEI-impregnated $MgCO_3$ showed the highest adsorption capacity of 1.07 mmol/g under try condition and around 19.7% enhancement in the presence of 10% H_2O at 75 °C.

3.2.6. Amine-loaded natural clays

Many minerals are suitable supports because of their high surface areas, good channel structures, low costs, and availability in nature. Liu et al. [110] investigated the adsorption capacity of DETA-impregnated, acid-activated sepiolite for CO_2 capture. At an optimal DETA loading of 80 wt%, the CO_2 adsorption capacity reached 1.65 mmol CO_2/g for 100% CO_2 at 35 °C. Chen et al. [109] modified kaolinite with amines to improve their adsorption capacities. They observed that 50% 4MEA+1EDA-modified kaolinite had the best CO_2 adsorption capacity of 149 mg/g (3.39 mmol/g-sorbent) due to chemisorption between the introduced amine and CO_2, compared with 3.3 mg/g for the pristine kaolinite. Thouchprasitchai et al. [111] investigated the adsorption capacity of TEPA-loaded hydrotalcite (b-cHT) at atmospheric pressure. The sorbent's maximum adsorption capacity was 6.1 mmol/g-sorbent at 80 °C in 30% CO_2/He. Stevens et al. [32] measured the adsorption capacities of diamine-modified montmorillonite at different conditions. The maximum adsorption capacities were 2.4 mmol/g-sorbent at 100 °C and 1.8 mmol/g-sorbent at 95 °C under 100% CO_2 and 15% CO_2/N_2, respectively. Regeneration cycles showed a 6.8 and 83% drop in the working capacity after nine runs with or without SO_2, respectively. Gómez-Pozuelo et al. [176] tested a series of amine-loaded clays (montmorillonite, bentonite, saponite, sepiolite, and palygorskite) by grafting, impregnation and double functionlization. Unlike amine-loaded mesoporous materials, double-functionalized clays displayed poorer CO_2 adsorption properties compared to their grafting- and impregnated counterparts due to pore-blocking problems related to their high organic loading.

4. Nitrogen-doped adsorbents

Unlike amine-loaded adsorbents, the CO_2 adsorption capacities of nitrogen-doped carbons are improved by increasing the number of alkaline-containing adsorption sites in carbon materials. Even though physical adsorption is the dominant process for these adsorbents, the abundant nucleophilic N sites improve sorbent CO_2 affinity, leading to higher CO_2/N_2 selectivity. Materials such as carbon, MOFs, and polymers can be doped by introducing N sources to the raw supports. The adsorption mechanisms and other performances of nitrogen-doped adsorbents have been widely discussed previously [7, 23, 24, 26]; therefore, only certain characteristics are reviewed in this section. The adsorption capacities and regeneration abilities of these adsorbents are summarized in Table 6.

Table 6. CO_2 adsorption performance of N-doped adsorbents

Materials	N source	CO_2 adsorption capacity (mmol/g-sorbent)[a]			Adsorption conditions	Desorption conditions	Cyclic ability[b]	Ref.
		25 °C	50 °C	75 °C				
KOH-petroleum coke	N_2	4.40			100% CO_2			[44]
Coconut shell	N_2	4.80			100% CO_2			[177]
N-doped MC	-NH_2, -NR_2	3.2			100% CO_2			[178]
N-doped PC	-NH_2	3.7			100% CO_2			[179]
N-doped HPC	Melamine	3.96 (0)			100% CO_2			[180]
Zn-aminotriazolato-oxalate	Atz	3.78			100% CO_2			[181]
ZTF-1	5-AT	5.6			100% CO_2			[182]
CAU-1	$H_2N–H_2BDC$	3.5			100% CO_2			[21]
NH_2-MIL-101(Al)	2-amino terephthalic acid	7.5			100% CO_2			[183]
$Cu_{24}(TPBTM^{6-})_8$-$(H_2O)_{24}$	TPBTM	23.53			CO_2, 20 MP			[184]
NPAFs	-NR_2	2.61			100% CO_2			[185]
Lewatit VP OC 1065	-NH_2		1.3		10% CO_2/N_2	120°C, N_2	7.69%,18	[98]
PMMA	Arg/PSS	1.3			100% CO_2			[174]
$MOF_{NH2: powder}$	-NH_2, -NHR	1.25	1.60	1.70	100% CO_2			[49]
$MOF_{NH2: powder}$	-NH_2, -NHR	1.09			15% CO_2/N_2	120°C, N_2	0%, 12	[49]

a Adsorption temperatures other than 25, 50 and 75 °C are included in brackets

b The notation marked as A%, B: A= declining value of adsorption capacity, B= total cycle number

4.1. Nitrogen-doped carbon materials

Nitrogen doping can be achieved either by ammoxidation or direct synthesis. Both microwave irradiation and traditional heating can be used for the ammoxidation process [29, 44]. Hu’s team [44, 177] synthesized nitrogen-doped carbonaceous CO_2 sorbent combined with urea modification, KOH activation and ammoxidation processes, successively. The sample prepared at 650 °C with a KOH/precursor ratio of 2 showed the highest CO_2 uptake and CO_2/N_2 selectivity. The high adsorption capacity under low temperature suggests that nature of the adsorption is physical. The fast adsorption rates and good regeneration ability, along with the sound adsorption capacity, confirmed this sorbent’s potential in capturing CO_2 from flue gases.

The direct synthesis process can be shortened by carefully selecting the precursors, templates, and activators. Templates specifically control the pore structures of the adsorbents obtained. Wei et al. [178] developed a controllable, one-pot method to synthesize N-doped mesoporous carbons. Using dicyandiamide as a nitrogen source, soluble Resol as a carbon source, and triblock copolymer F127 as a soft template, the sorbents were produced via a self-assembly process induced with solvent evaporation. The physical properties of the sorbents were adjusted by altering the mass ratios of these three components. The preferred adsorbents possessed tunable mesostructure, a pore size of 3.1–17.6 nm, a high surface area of around 494–586 m^2/g, a high N content up to 13.1 wt%, and high CO_2 capture of 2.8–3.2 mmol/g-sorbent at 25 °C and 100 kPa. Zhang et al. [179] synthesized N-doped porous carbon using PEI as the liquid carbon precursor and KOH as the activator. Due to the microporosity offering a high specific surface area, the rich nitrogen content, and various nitrogen functional groups, the adsorbents had a CO_2 uptake of 4.9–5.7 and 2.9–3.7 mmol/g-sorbent at 0 and 25 °C, respectively, and 100 kPa. Bing et al. [180] obtained N-doped hierarchical porous carbons via a template-free method by direct carbonization of melamine–resorcinol–terephthaldehyde networks. With a large specific surface area of 1150 m^2/g and a high nitrogen content of 14.5% generated from the interconnected 3D network, the highest CO_2 adsorption capacity reached was 3.96 mmol/g-sorbent at 0 °C and 100kPa. Similar N-containing materials have been synthesized via direct carbonization by other research groups [186-188]. In summary, N-doped adsorbents have similar properties to non-N-containing porous solid adsorbents. The only difference was the slightly higher isosteric heats of adsorption of around 30–44 kJ/mol, which demonstrate the good affinity between CO_2 and their N-based adsorption sites [189-191].

4.2. Nitrogen-doped MOFs

Nitrogen-doped MOFs include porous Zn-aminotriazolato-oxalate (ZAO), ZTF-1, CAU-1, MIL-101(Al), and N-doped porous aromatic frameworks (NPAFs). They are synthesized using compounds of zinc ($Zn(NO_3)_2 \cdot 6H_2O$), aluminum ($AlCl_3 \cdot 6H_2O$) or magnesium as the metal core, and amine-containing triazole, tetrazole, H_2BDC, terephthalic acid, and imidazole compounds as the organic framework [21, 181-183, 185]. Of these, Al-MOF MIL-101(Al) showed the highest adsorption capacity of 7.5 mmol/g-sorbent at 25 °C and 100 kPa, due to its extremely high surface area, rich N sites, and exceptional thermal and hydrothermal stability [183]. Kim et al. [49] synthesized alkylamine-containing MOFs using a one-step self-assembly process, and they showed similar features to the amine-loaded adsorbents. The adsorption capacity increased with temperature and reached 1.4 mmol/g-sorbent at 100 °C, attributed to active chemical interactions between the amine groups and CO_2 molecules. The CO_2

adsorption ability of powdered adsorbent was maintained over 11 repeated cycles. Darunte et al. [96] investigated the adsorption capacity and stability of amine-loaded mmen-M_2(dobpdc) (M=Mg and Mn) under humid conditions. A capacity of 3.25 mmol/g-sorbent was reached in a gas mixture of 10% CO_2 in He. Subsequently, the Mg_2(dobpdc) film was coated on a 100 CPSI cordierite honeycomb monolith for further scale-up. The CO_2 adsorption capacities reached 2.35 and 2.80 mmol/g-sorbent under 10% CO_2 in helium and pure CO_2, respectively, and 95% of the capacity was maintained over four adsorption–desorption cycles.

4.3. Nitrogen-doped polymers

For nitrogen-doped polymers, Hu et al. [101] prepared melamine-based microporous organic polymers via a one-pot polymerization process using the Schiff base reaction, and then investigated their CO_2 adsorption capacities. Owing to the N sites in the polymers and their microporous nature, the sorbents' capacity reached 2.8 mmol/g-sorbent at 0 °C and 118 kPa, and showed a high selectivity of 83.7 for CO_2 over nitrogen. Kitchin's group [31, 98] tested the CO_2-adsorption capacity and regeneration ability of a primary amine-loaded polymeric ion exchange resin (IER) named Lewatit VP OC 1065, produced by Lanxess under different temperatures and gas conditions. With repeated primary benzyl amine groups, the resin exhibited a good CO_2-adsorption capacity in the range of 1–2.5 mol/kg-sorbent depending on the partial pressure of CO_2 and the adsorption temperature, showed good regeneration ability, and had a low water adsorption capacity of 1.5 mol/kg-sorbent. Under more realistic conditions where the gas contained SO_2, the adsorption capacity of the sorbents decreased permanently. However, treatment with 1.5 M NaOH for three days partially recovered the CO_2-adsorption capacity due to the removal of sulfur.

In a follow-up study, Yu et al. [192] confirmed that Lewatit VP OC 1065 was thermally and hydrothermally stable up to 150 °C. However, its thermal stability at 70 °C under oxygen and at 120 °C under concentrated dry CO_2 was lower, due to the significant oxidative degradation of amine. The optimal flow rate of nitrogen for purging and regeneration temperature were also evaluated by calculating the total cost (includes the costs of purging and IER) and energy consumptions at different temperatures. A minimum total cost of 151 €/ton-CO_2 and the total energy of 7.5 GJ/ton-CO_2 were achieved at 100 °C under a flow rate of 1.00 L/min.

5. Opportunities and challenges

To date, most studies of NFSAs are still at an early stage. Even for the most widely studied silica adsorbents, research regarding industrial applications is still rare. For directly synthesized MOFs and polymers, current research is still at the stage of selecting materials and determining optimal adsorption conditions. In the future, there will be two possible aspects to developing NFSAs. One is to overcome their drawbacks to make them more competitive than aqueous amines; the other is to study their practical applications.

One of the drawbacks of amine-loaded adsorbents restricting their further applications is amine loss after long-term operation, which decreases adsorption capacity. There are different strategies to solve this problem for both amine-grafted and N-doped amine-loaded adsorbents. The amine retention ability of amine-grafted adsorbents can be improved by developing adsorbents with stronger bond forces between the amine molecules and the supports. Supports with various surface groups, such as polymers, may be suitable for grafting amines. Additionally, innovative grafting methods other than silane chemistry can be used in this process. Preventing amine loss in amine-impregnated adsorbents is more difficult, as there is no substantial chemical bond between the amine molecules and the supports. Therefore, there may be room for the development of support materials with special structures, such as the cage-like structures of zeolites used in the ship-in-a-bottle method described in Section 3.2.2., which can trap the macromolecular amines in their pores. For N-doped adsorbents, the main drawback is the difficulty to control the adsorption capacity via selecting materials or improving the synthesis process. This may be achieved using computer technology to guide the synthesis of better adsorbents and define their adsorption kinetics and thermodynamics. Drawbacks like oxidative degradation of amines, irreversible adsorption of SO_2, NO_2 and steam-induced degradation of the porous supports can be solved either by elimination these impurities before CO_2 capture or by developing adsorbents with oxidation-stability, SO_2, NO_2 resistant-ability and hydrothermal stability, respectively.

Further studies on the practical applications of NFSAs highly depend on abundant experimental and industrial data at different scales. The development of experimental instruments and technical processes adaptable to existing power-plant systems may be the main research direction. Cost reduction is another factor that should be considered for NFSA commercialization.

6. Conclusions

Solid adsorbents modified with N-containing functional groups have gained attention over recent decades due to their excellent CO_2 adsorption performance, high selectivity over many gases, low energy consumption, and good regeneration ability.

The techniques involved in the preparation of NFSAs can be used to develop two distinct types of adsorbents: amine-loaded and N-doped. In the former, amines or N-groups are loaded onto the surfaces of the solid supports. In the latter, N-containing adsorbents are directly synthesized by using amine precursors or treating the supports with N under high temperatures.

Silica, carbon-based materials, MOFs and other organic frameworks, polymers, zeolites, metallic compounds, and natural clay materials, which have large pore volumes and abundant hydroxyl groups on the surface, are all promising supports for amine loading. The adsorption capacities of post-synthesized NFSAs are high due to chemisorption between CO_2 and amines. The main strategies to improve the adsorption performances of amine-loaded adsorbents include:

1) Screening suitable amines for the synthesis of adsorbents with higher adsorption capacities or lower desorption temperatures. Mixed amine-loaded materials usually have better performance.

2) Improving the characteristics of supports by enlarging the pore sizes with specific reagents or choosing suitable additives and solvents, and applying appropriate treatment methods, such as solvent extraction or calcination.

3) Selecting supports with larger pore volumes and pore sizes for amine-impregnated adsorbents, or with abundant hydroxyl groups on the surface for amine-grafted adsorbents. Supports with hierarchical pore structures or multilayered structures are more suitable, while supports with fewer reactive surface sites are better for amine distribution.

4) Using unique, structured supports, such as cage-structured zeolites. Usually this

kind of sorbent possesses good adsorption capacities at moderate temperatures of 40–120 °C, excellent regeneration abilities and selectivity over nitrogen, and good endurance in the presence of water.

Aside from adsorption performance, cost needs to be considered, especially for large-scale applications. Therefore, cheap materials that are abundant in nature, such as clay, are preferred as adsorption supports.

High-temperature treatment in N_2 is a unique method to enrich the N sites on carbon materials for CO_2 adsorption. Synthetic supports, on the other hand, such as MOFs and polymers, can all be doped with N during the synthesis stage by introducing the amine-containing precursors. N-doped adsorbents usually have rich microporous structures, large surface areas, and abundant N sites. Like other porous solids, N-doped materials possess higher adsorption capacities at lower temperatures due to physical adsorption. Of the adsorbents mentioned, N-doped MOFs and polymers have the most promising future.

Conflicts of interest

There are no conflicts of interest to declare.

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