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# A brief on tetraethylenepentamine (TEPA) functionalized-adsorbents in CO<sub>2</sub> capture application

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**Abstract.** Among numerous carbon capture technologies, adsorption is considered one of the most effective approaches to reduce carbon dioxide (CO<sub>2</sub>) emissions in the atmosphere. Various modification approaches of adsorbents have been introduced to enhance the CO<sub>2</sub> adsorption ability. Recently, an amine such as tetraethylenepentamine (TEPA) has been extensively used as an adsorbent's promoter because of its high amine density, low viscosity, low cost, and low toxicity properties. This has added an advantage to the adsorbent in terms of economical and environmentally benign. Therefore, it is important to provide the latest review on TEPA-functionalized adsorbents, specifically on the effects of TEPA functionalization, different TEPA loading, diverse adsorption conditions, as well as the structure of adsorbents towards the CO<sub>2</sub> adsorption capacity. Different adsorption conditions over a wide range of adsorption temperatures were thoroughly discussed and several recommendations for future studies were also been proposed.

## 1. Introduction

Nowadays, as the technology in the century is getting more advanced, more energies are needed for the operation of various sectors, especially in the industrial sectors such as factories and chemical plants. According to the statistics, approximately 70 percent of total global greenhouse gas emissions are from the combustion of fossil fuels, cement production, and other industrial processes (1). These processes are accompanied by high emissions of CO<sub>2</sub>, which is a primary greenhouse gas responsible for climate change and global warming (2). Kamran and Park have stated that the amount of CO<sub>2</sub> in the atmosphere has increased from 280 to 410 ppm as the world temperature has risen from 273.6 to 274 K (3). A study conducted by Alkadhem and co-workers has demonstrated that the average Earth temperature will rise by about 274.5 K in this century (4). It is anticipated that the environment and the lives of many species will be adversely impacted if the global warming problem remains severe for the next few decades. Besides, the increment of worldwide global warming also inevitably could result in oxygen depletion and subsequent plankton extinction (5).

In this regard, researchers and concerned industries have been desperately seeking ways to reduce CO<sub>2</sub> emissions to the atmosphere. One of the ways is Carbon Capture and Storage (CCS), a simple approach where it involves the capturing, transporting, and storing of the CO<sub>2</sub> (6). The CCS technologies that are currently available include absorption, adsorption, cryogenic, membrane processes, etc (7). Different from the adsorption process that occurs on the surface, the absorption includes the whole material or liquid volume (6). However, the adsorption technique possesses some advantages such as the high loading capacity at ambient conditions, lower energy demand, and economic regeneration (8).



To date, several adsorbents have been extensively studied such as zeolites, carbon, silica, metal oxide, and metal-organic-frameworks (MOFs) (7). Numerous modification techniques were also reported that could further enhance the CO<sub>2</sub> adsorption performance of these adsorbents.

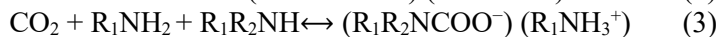
Among these approaches, amine-functionalized solid sorbents have attracted more attention for CO<sub>2</sub> capture applications (2). This is because the combination of high CO<sub>2</sub> affinity of amines and porous materials will exhibit beneficial properties such as high CO<sub>2</sub> adsorption rate and high thermal stability (9). Different from aqueous amine absorbent, the resultant amine-functionalized solid adsorbents did not require a large amount of energy for the regeneration process. These types of adsorbents also have high CO<sub>2</sub> adsorption capacity and could prevent the corrosion problem of equipment which is caused by the use of highly concentrated aqueous amine absorbent (9). In the previous studies, a few types of amines were employed and their effects toward improving the CO<sub>2</sub> uptake capacity of solid adsorbent were thoroughly investigated. These include several types of organic amines such as diethylenetriamine, triethylenetetramine, and TEPA. TEPA is a low cost, low toxicity, and high molecular weight amine with multiple amine groups per molecule (two primary amines (RNH<sub>2</sub>) and three secondary amines (R<sub>2</sub>NH) groups) (10, 11). Besides, TEPA as a branched polyamine has abundant amino functional groups and could potentially enhance the CO<sub>2</sub> adsorption of solid porous inorganic substrates such as nanosepiolite and mesocellular silica sponge (12). Furthermore, TEPA has a higher density of amine groups and a relatively lower viscosity compared to other amine compounds (13).

In this review article, an attempt has been carried out focusing on TEPA-functionalized adsorbents used for CO<sub>2</sub> capture applications. The effects of TEPA functionalization, different TEPA loading, and diverse adsorption conditions over a wide range of adsorption temperatures, as well as the impact of adsorbent's structure towards CO<sub>2</sub> uptake capacity, are also covered in this review. The future opportunities for the study of TEPA-functionalized adsorbents are finally presented to stimulate interest in this interesting area of CO<sub>2</sub> capture application.

## 2. Discussion

### 2.1. TEPA-functionalized adsorbents in CO<sub>2</sub> capture application

Recently, TEPA has been investigated as one of the amine alternatives for the functionalization of adsorbents toward effective CO<sub>2</sub> capture. TEPA are a linear molecules with five amine moieties that consists of two kinds of amine groups that are primary (R<sub>1</sub>-NH<sub>2</sub>) and secondary (R<sub>1</sub>-NH-R<sub>2</sub>) amines (9, 14). This properties of TEPA have proved the enhancement in the TEPA-functionalized adsorbents during CO<sub>2</sub> adsorption. Many researchers have subsequently concentrated on TEPA- functionalized sorbents as this type of amine offers promising advantages, such as higher density of amine groups and a relatively lower viscosity compared to other amine compounds. For example, based on the paper by Kasikamphaiboon and co-workers, during the adsorption of CO<sub>2</sub> into the MgO adsorbents, carbamates have been formed between two amine groups based on the chemical equations (1)-(3) below (9):



In the raw MgO adsorbent, less CO<sub>2</sub> molecule can be adsorbed on to the solid surface, due to the lack of active sites. However, in the TEPA-functionalized MgO adsorbent, the amine groups available in TEPA molecule has provided more active sites for CO<sub>2</sub> adsorption and more alternative pathways for the MgO/CO<sub>2</sub> reaction (7).

Table 1 shows a summary of raw adsorbents and TEPA-functionalized adsorbents prepared using different synthesis methods used for CO<sub>2</sub> capture application.

**Table 1.** A summary of raw adsorbents and TEPA-functionalized adsorbents prepared using different synthesis methods used for CO<sub>2</sub> capture application.

Synthesis Method	Adsorbent	BET Surface area (m <sup>2</sup> /g)	BJH Pore volume (cm <sup>3</sup> /g)	Temperature (K)	Pressure (atm)	Adsorption flow condition (CO <sub>2</sub> :%inert gas%)/%H <sub>2</sub> O	CO <sub>2</sub> uptake (mmol/g)	Stability (mmol/g)	Ref.
Gel-casting method	MM-550	1088.3	1.00	348	1	(100:-)/-	0.65	-	(15)
Gel-casting + Impregnation method	MM-550-TEPA-	10.5	0.02	348	1	(100:-)/-	3.43	3.33 (5 <sup>th</sup> cycle)	
						(12:88 N <sub>2</sub> )/-	3.18	2.95 (5 <sup>th</sup> cycle)	
Rapid Synthesis method	AlFu	828.4	0.436	348	1	(15:85 N <sub>2</sub> )/- (100:-)/-	0.19 0.74	- -	(1)
Rapid Synthesis + Wet Impregnation method	AlFu-TEPA-	20.2	0.060	348	1	(15:85 N <sub>2</sub> )/-	3.59	-	
						(100:-)/-	4.1	3.87 (10 <sup>th</sup> cycle)	
Improved Hummers' method	GO	289.028	0.046	338	0.09	(10:90 He)/-	0	-	(16)
Improved Hummers' + Ultrasound	GO-TEPA	194.484	0.042	338	0.09	(10:90 He)/-	1.2	1.08 (10 <sup>th</sup> cycle)	
Activation + Chemical Grafting method									
Pre-oxidation method	HMC	480.88	0.74	333	-	(15:85 N <sub>2</sub> )/-	-	-	(13)
Pre-oxidation + Wet Impregnation method	HMC-TEPA-	38.33	0.16	333	-	(15:85 N <sub>2</sub> )/-	1.42	-	
						(15:85 N <sub>2</sub> )/5	1.46	-	
						(15:85 N <sub>2</sub> )/10	1.54	-	
						(15:85 N <sub>2</sub> )/15	1.67	1.51 (10 <sup>th</sup> cycle)	
						(15:85 N <sub>2</sub> )/19	1.60	-	
Zinc Nitrate Hexahydrate method	MOF-177 powder	2784	1.34	298	1 bar	(100:-)/-	0.86	-	(14)
	MOF-177 pellet	2784	1.34	298	1 bar	(100:-)/-	0.57	-	
Zinc Nitrate Hexahydrate + Wet Impregnation method	MOF-177-TEPA-powder	585	0.330	298	1 bar	(100:-)/-	3.82	-	
	MOF-177-TEPA-pellet			298	1 bar	(100:-)/-	3.31	108.2 wt% (12 <sup>th</sup> cycle)	
Pluronic P123 + Tetraethyl Orthosilicate method	SBA-15(p)	189.46	0.44	348	-	(20:80 N <sub>2</sub> )/-	0.61	-	(17)
Pluronic P123 + Tetraethyl Orthosilicate + Wet Impregnation method	SBA-15(p)-TEPA-	2.16	0.007	348	-	(20:80 N <sub>2</sub> )/-	5.39	5.0 (9 <sup>th</sup> cycle)	
Sol-gel method	MgO	207	0.81	303	-	(40:60 N <sub>2</sub> )/-	0.95	-	(9)

Sol-gel + Wet Impregnation method	MgO-TEPA	19	0.22	303	-	(40:60 N <sub>2</sub> )/-	4.98	4.71 (10 <sup>th</sup> cycle)	
Acid Leaching method	FSA	541	0.543	298	1 bar	(5:95 gas)/- inert	0.52	-	(18)
Acid Leaching + Physical Impregnation method	FSA-TEPA	185	0.25	298	1 bar	(5:95 gas)/- inert	1.32	1.18 (10 <sup>th</sup> cycle)	
Organic Template method	ZSM-5	398.660	0.442	373	1	(100:-)/-	0.22	-	(19)
Organic Template + Wet Impregnation method	ZSM-5-TEPA	19.045	0.049	373	1	(100:-)/-	1.80	1.53 (5 <sup>th</sup> cycle)	
Polyethyleneglycol method	HPS	978.7	2.19	348	1	(10:90 N <sub>2</sub> )/- (15:85 N <sub>2</sub> )/-	1.49 0.56	-	(20)
Polyethyleneglycol + Typical Impregnation method	HPS-TEPA-	20.32	0.15	348	1	(15:85 N <sub>2</sub> )/-	5.01	4.7 (10 <sup>th</sup> cycle)	
Polystyrene Templates method	MHSS	1139	0.284	-	1	(30:70 N <sub>2</sub> )/-	0	-	(21)
Polystyrene Templates + Wet Impregnation method	MHSS-TEPA	33	0.082	-	1	(30:70 N <sub>2</sub> )/-	10.37	-	
Microemulsion Templating method	MCF-0.8	703.36	1.59	348	-	(15:85 N <sub>2</sub> )/-	0	-	(22)
Microemulsion Templating + Wet Impregnation method	MCF-0.8-TEPA	6.68	0.04	348	-	(15:85 N <sub>2</sub> )/- (15:85 N <sub>2</sub> )/5	4.75 5.26	4.46 (10 <sup>th</sup> cycle) 4.91 (10 <sup>th</sup> cycle)	
Potassium Hydroxide method	MCNT	169.8	1.97	333	-	(10:90 N <sub>2</sub> )/1	-	-	(23)
Potassium Hydroxide + Wet Impregnation method	MCNT-TEPA	2.2	0.03	333	-	(10:90 N <sub>2</sub> )/1	5.00	4.00 (10 <sup>th</sup> cycle)	
Hydrothermal method	PE-KIT-6	207.61	0.72	333	-	(15:85 N <sub>2</sub> )/-	0.94	-	(24)
Hydrothermal + Post-synthetic Impregnation method	PE-KIT-6-TEPA	20.48	0.08	333	-	(15:85 N <sub>2</sub> )/-	2.9	-	
Hydrothermal method	TiO <sub>2</sub> /NRs	235	1.16	313	1 bar	(100:-)/-	0.76	-	(25)
Hydrothermal + Wet Impregnation method	TiO <sub>2</sub> /NRs-TEPA	50	0.43	313	1 bar	(100:-)/-	2.29	2.16 (12 <sup>th</sup> cycle)	

MM-550: Monolithic MCM-41 (Mesoporous silica) at 550°C calcination temperature

AlFu: Aluminium fumarate metal-organic framework

GO-TEPA: Graphene oxide-TEPA under ultrasound irradiation

HMC: Hierarchical mesoporous carbon

MOF-177: Metal organic framework-177

SBA-15(p): Mesoporous silica with pluronic P123

MgO-TEPA: Magnesium oxide-TEPA under biogas (38.4% CO<sub>2</sub> and 61.5% CH<sub>4</sub>)

FSA: Fine Slag Adsorbent

ZSM-5: Zeolite Socony Mobil-5

HPS: Hierarchically porous silica

MHSS: Mesoporous hollow silica spheres

MCF-0.8: Mesocellular silica foams with 0.8 molar ratio of 1,3,5-trimethylbenzene (TMB) to P123

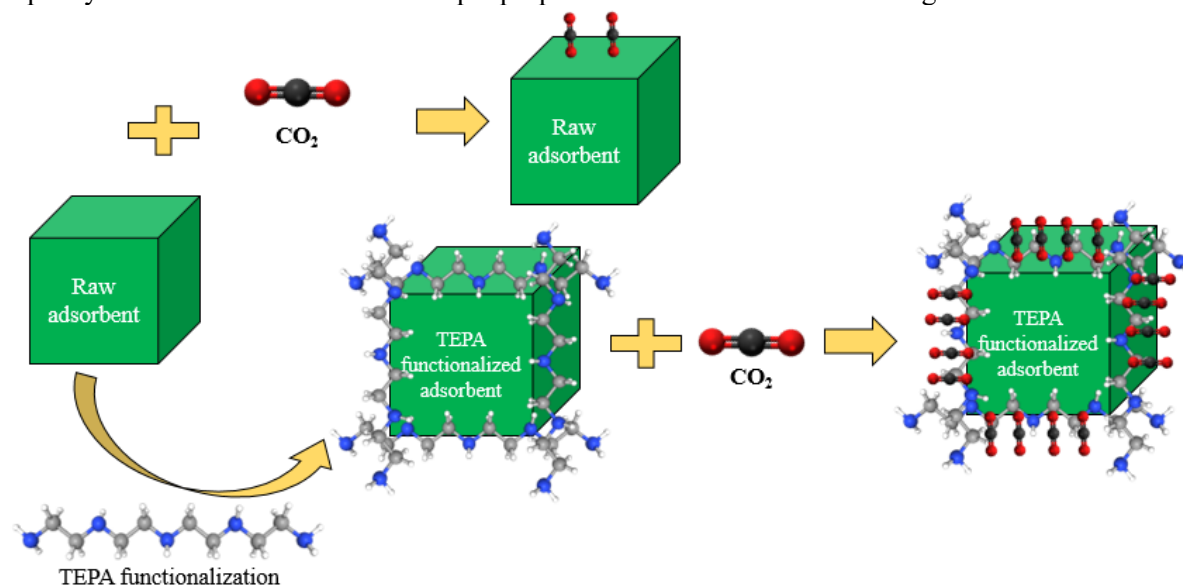
MCNT: Modified carbon nanotubes

PE-KIT-6: Mesoporous silica pore-expanded KIT-6

TiO<sub>2</sub>/NRs: TiO<sub>2</sub>/titanate composite nanorod

## 2.2. The effect of TEPA functionalization towards CO<sub>2</sub> uptake capacity

Numerous studies have verified that the impregnation of TEPA has contributed to a better CO<sub>2</sub> uptake capacity of the solid adsorbents. A simple proposed mechanism is shown in Figure 1.



**Figure 1.** Proposed mechanism of CO<sub>2</sub> adsorption over a raw adsorbent and a TEPA-functionalized adsorbent.

According to previous studies, the decrease in BET surface areas and pore sizes of the modified sorbents (Table 1) could be observed, suggesting that the TEPA molecules have been successfully loaded onto the sorbents' surface and pore volume. It could also be perceived that the CO<sub>2</sub> uptake capacity of TEPA-functionalized adsorbents is much higher than that of raw adsorbents. For instance, the CO<sub>2</sub> adsorption capacity of MM-550-TEPA-70% was significantly increased to 3.43 mmol/g after the impregnation of TEPA, as compared to the raw MM-550 (0.65 mmol/g) (15). As a matter of fact, the adsorption process of raw MM-550 adsorbent is the physical adsorption type. After impregnating with 70% TEPA, the participation of the chemical reaction between the amine-functional groups and the CO<sub>2</sub> molecular has provided more active sites for eased CO<sub>2</sub> molecule capture. Moreover, upon TEPA-functionalization, the resultant modified graphene oxide (GO) has demonstrated a high CO<sub>2</sub> adsorption capacity (1.2 mmol/g) than pure GO (0 mmol/g) at 338K and 0.09 atm (16). In this study, ultrasound irradiation is used to exfoliate the graphene layers and produce more available active sites to attach the amine functional groups to the graphene matrix.

On the other hand, aside from N<sub>2</sub> adsorption-desorption isotherm investigated on the after effect of the amine functionalization, other characterisation analysis also able to demonstrate the differences result from the success of the TEPA-functionalization approach onto the solid support. As the evidence of the XRD analysis in the study from Kasikamphaiboon and co-workers, by comparing the diffraction pattern of MgO with those of MgO-TEPA-x with different TEPA loadings, it can be observed that the diffraction intensity of MgO decreases with increasing TEPA loadings (9). It has been known that diffraction intensities are relative to the degrees of pore filling. Therefore, the loss of intensity is possibly caused by the incorporation of amine into the pore channels of the support. This indicates that TEPA is successfully loaded into the pore of the raw MgO adsorbent, which found in-line with other amine-functionalization related studies. The study have also proved that the functionalization of TEPA into MgO adsorbent has significantly improved the CO<sub>2</sub> uptake capacity (9). In fact, the CO<sub>2</sub> adsorption of the pristine MgO reaches the saturation point within only 12 min, resulting in a low adsorption capacity

of 0.95 mmol/g. As expected, after impregnating with TEPA, the adsorption capacity expressively increases to a promising value (4.98 mmol/g). Similarly, the TEPA-modified pore-expanded KIT-6 has shown a higher CO<sub>2</sub> capture capacity (2.9 mmol/g) than that of raw PE-KIT-6 (0.94 mmol/g). (24). The addition of TEPA on titanate-TiO<sub>2</sub> composite has also enhanced the CO<sub>2</sub> uptake capacity to 2.29 mmol/g (25). From the abovementioned studies, it is believed that the enhanced adsorption performance of the TEPA-functionalized adsorbents is due to the presence of beneficial interaction between -NH<sub>2</sub> groups of the loaded amines and CO<sub>2</sub> that significantly aided the CO<sub>2</sub> uptake.

It is noted that there are 2 different functionalization methods of TEPA into the raw adsorbents, namely impregnation method and grafting method. In the former, amine is immobilized in the channel of solid adsorbents by van der Waals forces (26). Wet impregnation method is widely used as it is the easiest way of placing amines on solid surfaces (27). By using this method, amines are mixed with the support material by the help of a solvent. Then, by evaporation of the diluted solution, the excess solvent is removed. On the other hand, for grafting method, CO<sub>2</sub>-philic sites are immobilized by chemical bonds through the condensation of alkanolamine and silanol groups (26). During the grafting of amine into solid adsorbents, a covalent bond is formed between the amine chains and the surfaces formed by the reaction of the silanol groups with the silanes on the chain (27). In this method, the amount of amine that can be doped into the support material is dependent on the density of the appropriate silanol groups. In terms of advantages, wet impregnation method can be prepared practically, has high amine capacity and decreased corrosion behaviour (27). In the case of grafting method, the strong chemical bond of the amines is advantageous because high temperature is required to break the bonds, thus increasing the amine-grafted adsorbents' thermal stability (27).

### *2.3. The effect of different TEPA loading towards CO<sub>2</sub> uptake capacity*

It is well-recognized that the diverse amine loadings including TEPA could suggestively affect the CO<sub>2</sub> capture performance. It was previously reported that the increase in TEPA loading within a suitable range has increased the breakthrough time and adsorption capacity of the adsorbents, as more amine active sites for CO<sub>2</sub> adsorption, are provided (9). However, the excess TEPA loading has led to the blockage of the pore of adsorbents by the aggregated TEPA, which hinders the diffusion of CO<sub>2</sub> to react with the active sites in the pores. As the optimum TEPA loading, 40% MM-550-TEPA has shown the maximum breakthrough time and adsorption capacity of 34 min and 4.98 mmol/g, respectively. In a similar study, it was verified that the increasing of TEPA loading has increased the CO<sub>2</sub> adsorption capacity of MM-550 adsorbent (15). Herein, the optimum TEPA loading is 70% with the highest adsorption capacity of 3.43 mmol/g at pure CO<sub>2</sub> gas, and a further increase of TEPA to 75% has led to a decrease in the CO<sub>2</sub> adsorption capacity.

In a study by Zhang et. al., an increasing trend in CO<sub>2</sub> uptake capacity was observed upon increasing the TEPA loading from 10% to 20%, and as expected, a further increase of TEPA amount to 30% and above have caused the decreasing trend (18). As the optimum TEPA amount, 20% FSA-TEPA has demonstrated an adsorption capacity of 1.32 mmol/g. In order to investigate the effect of TEPA loadings on the CO<sub>2</sub> capture of mesoporous hollow silica spheres (MHSS), 9-52wt% of TEPA were impregnated onto MHSS adsorbents. It was perceived that the CO<sub>2</sub> adsorption capacity was increased from 3.01 to 10.37 mmol/g when the loading amount of TEPA was increased from 9 to 47 wt% (21). Nonetheless, a further increase of TEPA loading to 52wt% could not auxiliary increase the CO<sub>2</sub> adsorption capacity, most probably due to the aggregation of excessive TEPA amine on the MHSS support. This inevitably leads to a reduction in the accessibility of CO<sub>2</sub> inside the adsorbent porosity, thus decreased the performance.

### *2.4. The effect of different adsorption conditions towards CO<sub>2</sub> uptake capacity*

It is widely known that the different adsorption conditions have diversely impacted the CO<sub>2</sub> adsorption capacity. Similar to other amine groups, the TEPA-functionalized adsorbents have shown variation in CO<sub>2</sub> capture performance upon changing the adsorption reaction conditions. In this respect, the next

sections were provided to present the effect of those reaction conditions on the CO<sub>2</sub> uptake of numerous TEPA-functionalized adsorbents.

*2.4.1. Adsorption temperature.* As one of the important parameters, the temperature undoubtedly has a noteworthy effect on the CO<sub>2</sub> adsorption capacity (1). For instance, the CO<sub>2</sub> adsorption capability of AlFu decreases with the increase in the adsorption temperature. In the absence of TEPA, the CO<sub>2</sub> adsorption capacity of AlFu was only 0.27 mmol/g at 318 K. Upon addition of 50% TEPA, the CO<sub>2</sub> uptake amount is 3.4 mmol/g at 333 K and significantly increases to 3.59 mmol/g for AlFu-TEPA-60% at 348 K. From this observation, it could be concluded that the rising in the adsorption temperature can help the CO<sub>2</sub> molecules to overcome the kinetic barrier and reduce the diffusion resistance. However, as anticipated, the overloading of TEPA amount would negatively impact the overall performance by blocking the pore structures of AlFu and hinders the reaction between CO<sub>2</sub> molecules with the internal TEPA of modified AlFu.

Moreover, in another study, TEPA-functionalized SBA-15(p) has shown increased adsorption capacity from 4.41 to 5.39 mmol/g when the temperature rose from 323 K to 348 K. However, when the temperature reached 363 K, the adsorption capacity drastically dropped to 4.98 mmol/g (17). This is because when the adsorption temperature is higher than the optimal adsorption temperature, CO<sub>2</sub> uptake is controlled by thermodynamics and the CO<sub>2</sub> adsorption decreases with the temperature increase. In contrast, the CO<sub>2</sub> adsorption capacity of pure ZSM-5 was decreased with the increase of adsorption temperature [19]. After incorporation of low amine loading (ZSM-5-TEPA-3g), the CO<sub>2</sub> uptake was increased and then decreased with the increase of adsorption temperature. A different observation was observed when high amine loadings of ZSM-5-TEPA-5g, ZSM-5-TEPA-7g, and ZSM-5-TEPA-9g were used, in which the CO<sub>2</sub> adsorption was increased with the increase of adsorption temperatures. This can be explained by the fact that the ZSM-5 adsorption of CO<sub>2</sub> was a physical adsorption process and an exothermic reaction, a dissimilar condition to that of high TEPA loadings-ZSM-5.

Furthermore, in a study on hierarchically porous silica, HPS-TEPA-60% adsorbent has demonstrated the highest amount of CO<sub>2</sub> capture when the temperature increases to the optimum, and decreased upon a further increase in the temperature (20). This is most possibly due to the expansion of TEPA when a high temperature was used that might block the pore of the HPS support and increase the CO<sub>2</sub> diffusion resistance for retarded performance.

*2.4.2. Flow condition.* Liu and co-workers have conducted the CO<sub>2</sub> adsorption in pure CO<sub>2</sub> gases and mixture gases of 15% CO<sub>2</sub>, 85% N<sub>2</sub>, respectively (1). It was perceived that for both raw AlFu and modified adsorbent with different TEPA loadings, the CO<sub>2</sub> adsorption capacity under a pure CO<sub>2</sub> atmosphere is higher than that under a mixture of gases. Therefore, it could be summarized that a higher partial pressure of CO<sub>2</sub> leads to a superior amount of saturated CO<sub>2</sub> adsorption. When the concentration of CO<sub>2</sub> raised from 5 to 40 vol%, the saturated adsorption capacity of MCF-0.8-TEPA60% was increased (22). This is because when the mixed gases with high concentrations of CO<sub>2</sub> pass through the adsorbent, the content of CO<sub>2</sub> molecule per unit volume was raised, and thus more CO<sub>2</sub> molecules could quickly contact the adsorption sites in the pores. Other than the existence of the above-mentioned mixture gases, many impurity gases such as SO<sub>2</sub> and NO<sub>x</sub>, water vapor, and some other acid impurities might also be present in the flue gas. It was early reported that the CO<sub>2</sub> adsorption capability reduces from 5.26 to 4.64 mmol/g and the regeneration amount is only 3.85 mmol/g when the MCF-0.8-TEPA60% adsorbent is exposed to acid impurities. This result indicates that the acid impurities in the mixed gas have a negative influence on CO<sub>2</sub> adsorption and adsorbent regeneration properties of adsorbents.

*2.4.3. Moisture present.* From the study by Wang et. al., it was observed that the saturated adsorption capacity and TEPA efficiency of HMC-TEPA-30% are enhanced obviously in the presence of water vapor (13). When the water vapor content increased from 0 to 15 vol%, the reaction between amine groups with CO<sub>2</sub> and H<sub>2</sub>O was facilitated, thus increasing adsorption capacity and TEPA efficiency. However, the CO<sub>2</sub> adsorption capacity decreases as the water vapor content is further increased from 15



to 19 vol%. Similarly, a study by Irani and co-workers also stated that the addition of 1 vol% moisture has increased the CO<sub>2</sub> sorption capacity by 56% (3.2–5 mmol/g) compared to dry gas adsorption (23). In contrast, when the moisture concentration increased more than 1 vol%, the adsorption capacity decreased from 5 mmol/g to 3.5 mmol/g. In both works, the decrease in CO<sub>2</sub> uptake at high water content can be explained due to the presence of excess water molecules that unavoidably occupy the available adsorption sites, thus reducing the exposure to CO<sub>2</sub> molecules.

**2.4.4. Adsorbent structure.** A study by Gaikwad et. al. has suggested that the powder form of MOF adsorbent is not suitable for industrial applications even though it possesses a higher CO<sub>2</sub> adsorption capacity (0.86 mmol/g for raw MOF-177 and 3.82 mmol/g for TEPA-modified MOF-177) (14). This is because the MOF powders are easily moving and inevitably block the system under continuous fluid flow in a packed column. As a result, the CO<sub>2</sub> adsorption capacity of MOF-177-TEPA-20% pellet was decreased concerning that of TEPA-20% powder due to reduced crystallinity, condensed geometry, and pore blockage by polymer binder during pelletization under ambient pressure. In short, MOFs are normally isolated as crystalline powders that are not industrially favourable due to their limitations in processing. Shaping MOFs into different forms such as the pellet form while preserving or improving their properties is a better approach as they can be easily processed, handled, and stored (28).

### 3. Concluding remarks and future opportunities

In this work, the recent research progress of TEPA-modified adsorbents used for CO<sub>2</sub> adsorption has been comprehensively discussed. The impregnation of TEPA into various adsorbents has increased the CO<sub>2</sub> adsorption capacity of the modified adsorbents. Different TEPA loadings have diversely affected the CO<sub>2</sub> uptake capacity, in which the increase in TEPA loading to the optimum amount has also enhanced the adsorption capacity, due to the increased amount of amine functionalities. When the TEPA loading exceeds the optimum amount, the CO<sub>2</sub> adsorption capacities decrease since the surface area and pore volume are dominant factors governing the CO<sub>2</sub> adsorption capacity over the amine functionality of TEPA. Various temperatures also contributed to the CO<sub>2</sub> adsorption capacity of adsorbents. The free volume of TEPA in adsorbents increased when the temperature increased, hence eased the diffusion of CO<sub>2</sub> molecules into the inner layer of TEPA for faster CO<sub>2</sub> adsorption by the amine groups. Over the optimum temperature, the effect of heat became dominant over the increased free volume, thus decreasing the adsorption capacity. In addition, higher partial pressure of CO<sub>2</sub> gases during the adsorption process has increased the CO<sub>2</sub> capture capacity. The moisture present in the flow gas also improved the adsorption capacity, as long as it was within the optimum amount. Besides, the adsorbent structure is considered an important parameter in real-life applications. Nonetheless, there was a lack of studies regarding this matter. As discussed above, adsorbents in pellet forms might be a better option for industrial usage. The adsorption performance should also be evaluated under actual industrial conditions where impurities such as NO<sub>x</sub>, SO<sub>x</sub>, and air are present.

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