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ORIGINAL ARTICLE

Bifunctional Materials for CO_2 Adsorption: Short Review

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ABSTRACT – In recent years, there has been growing interest in adsorbents with high surface area, high porosity, high stability and high selectivity for CO_2 adsorption. By the incorporation of the additive on the supports such as zeolite, silica, and carbon, the physicochemical properties of the adsorbent and CO_2 adsorption performance can be enhanced. In this review, we focus on the overview of bifunctional materials (BFMs) for CO_2 adsorption. The findings of this study suggests that the high surface area and high porosity of the support provide a good medium for high dispersion and accessibility of additives (amine or metal oxide), enhancing the CO_2 adsorption efficiency. The excessive additive however may lead to a decrease of CO_2 adsorption performance due to pore blockage and the decrease of active sites for CO_2 interactions. The synergistic relationship of the supporting material and additive is significant towards the enhancement of CO_2 adsorption.

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INTRODUCTION

The increase in the human population on earth has resulted in a degradation of the environment. One of the problems to be faced is global warming. Carbon dioxide is the main greenhouse gas that causes this phenomenon. Therefore, the effort to capture CO_2 should be carried out as soon as possible either from the source of emission or from the earth's atmosphere. Currently, there are several technologies to capture CO_2 gases, namely pre combustion [1], post combustion [2], and oxyfuel combustion [3]. Among these three technologies, post combustion demonstrates the lowest minimum concentration of CO_2 gas emitted. In addition, this technology exhibits technical and economical advantages such as low energy requirements for regeneration, low capital operating costs, low amount of O_2 usage and less corrosion problems [4]. Hence, post-combustion technology is regarded as one of the promising technologies and has been widely used recently owing to high selectivity of adsorbent towards CO_2 gases.

There are several techniques for post combustion CO_2 capture such as absorption, adsorption, membrane, and cryogenics [5]–[7]. Absorption technique using aqueous amine, for instance monoethanolamine (MEA), diethanolamine (DEA), and piperazine [8]–[10] has been employed. However, this technique possesses several limitations such as solvent degradation, loss of solvent, and generation of volatile compounds [11]. Therefore, adsorption method is the preferred technique considering the practical benfits it offers including low energy requirement and high regeneration ability. Several solid adsorbents such as zeolite-based, silica-based, and carbon-based have been extensively studied on account of the properties as CO_2 adsorbent, primarily in their textural properties. However, these adsorbent materials need to be further modified with additives such as amines or metal oxides to increase their CO_2 affinity and further boosting their CO_2 adsorption capacity as well as CO_2 selectivity.

In this review, we focused on the bifunctional materials (BFMs) which are zeolite-based, silica-based, and carbon-based as a supporting material for additive loading (amines and metal oxides) towards CO_2 adsorption. To the best of our knowledge, there is a scarcity in review, reporting on the BFMs for CO_2 adsorption, particularly amines and metal oxide as additive. The synergistic effect of the BFMs towards physicochemical properties and CO_2 adsorption performance will be discussed. We believe that the synergistic effect between supporting material and additive increases the CO_2 affinity and CO_2 adsorption capacity.

BIFUNCTIONAL MATERIALS (BFMs)

Zeolite-Based Adsorbent

Recent studies show that zeolite demonstrates good affinity towards CO_2. Besides, the tuneable porosity is also one of the advantages to enhance the adsorption performance. Table 1 shows the physicochemical properties and CO_2 adsorption performance of zeolite based BFMs. Previously, Wang et al. [12] studied the effect of amine weight percent into ZSM-5 towards CO_2 adsorption. The results showed that the CO_2 adsorption capacity was increased by impregnating tetraethylene pentaamine (TEPA). However, small amount of TEPA is not suitable for CO_2 adsorption at high temperature due to physical interaction between CO_2 and ZSM-5 and the associated exothermic process may detach the trap of CO_2. Furthermore, the higher amount of TEPA creates pore blockage, thus decreasing the pore size. Therefore, 41 wt.% of TEPA showed the optimum CO_2 adsorption capacity of 1.80 mmol/g at 100 °C. Lee et al. [13] synthesized ZSM-5 with 5 different structure directing agents (TMA, TPA. TMA + TEA, TMA + TPA, TEA + TPA) for CO_2 adsorption. In this

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study, the effect of pore structure and weight percent of polyethylenimine (PEI) were examined. They found that the surface area and total pore volume are the governing factors for CO_2 adsorption. Moreover, ZSM-5 (TMA + TEA) showed the highest CO_2 adsorption attributed to the high surface area with larger micropore and smaller mesopore volume, which tends to form stronger electric field for CO_2 adsorption. In terms of effect of PEI loading (28.6, 33.3, and 37.5 wt.%), they found that ZSM-5 with high surface area and high total pore volume occupies more PEI loading, which resulted in high interaction of CO_2. To conclude, ZSM-5 (TMA + TEA) with 33.3 wt.% of PEI showed the highest CO_2 adsorption performance at 2.64 mmol/g. Wang et al. [14] studied the effect of metal ions in zeolite toward CO_2 adsorption. They observed that the exchange of transition metal ions increased the CO_2 adsorption capacity (3.32 mmol/g) due to small radius size of cation which prevents pore blockage. Gao et al. [15] found that the addition of 10.8 wt.% of Mg onto zeolite Y by solid state dispersion technique showed the optimum condition with CO_2 adsorption capacity of 2.78 mmol/g, at 30 °C and 4.93 atm. This indicates that the formation of monolayer MgO onto zeolite increased the active sites for CO_2 adsorption. However, increasing the Mg percentage above 10.8 wt.% led to the accumulation and pore blockage, decreased the number of active sites and CO_2 adsorption performance. Furthermore, they also found that MgO@zeolite-Y indicated a high CO_2 selectivity and stability for 10 cycles at 30 °C. Boruban and Nalbant Esenturk [16] studied the effect of CuO on zeolite towards CO_2 adsorption. They found that the addition of spiky and spherical CuO structure onto zeolite decreased the CO_2 physisorption from 2.62 mmol/g to 1.88 mmol/g and 2.16 mmol/g, respectively. This might happen due to the decrease in surface area and pore volume. On the other hand, the CO_2 chemisorption showed a steep increase from 1.61 mmol/g to 3.40 mmol/g for spiky, and 2.99 mmol/g for spherical-shape CuO. This phenomenon occurs due to tendency of CuO to chemically trap CO_2. Higher CO_2 chemisorption on spiky CuO compared to spherical CuO can be explained by the higher content of Cu particles as proven by AAS analysis. In a nutshell, we can conclude that a suitable synthesis method, optimum loading amount, and highly dispersion of additive are crucial for the improvement of CO_2 adsorption.

Table 1. Physicochemical properties and CO_2 adsorption of zeolite-based adsorbents.

Adsorbent	**Additive**		**BET Surface Area, (m^2/ g)**	**Total Pore Volume, (cm^3/g)**	**Temp. (°C)**	**CO_2 Adsorption Capacity, (mmol/g)**	**Ref.**
	Type	**wt.%**					
ZSM-5	TEPA	41.0	19	0.049	100	1.80	[12]
ZSM-5	PEI	33.3	329	0.116	40	2.64	[13]
ZSM-5	Zn	-	193	0.141	0	3.32	[14]
Zeolite Y	MgO	10.8	399	0.270	30	2.78	[15]
Zeolite Y	CuO	25.0	695	0.249	67 – 247	2.16	[16]

Silica-Based Adsorbents

Over the past decades, researchers have focused more on the silica-based adsorbent which posseses unique characteritics such as tuneable porosity, high surface area, and high stability. However, due to the poor affinity towards CO_2, the modification of silica-based adsorbent is urgently needed. Table 2 shows the physicochemical properties and CO_2 adsorption of silica-based adsorbent. Taheri, Ghaemi and Maleki [17] studied the effect of porosity and different loading amount of TEPA towards CO_2 adsorption. They found that the addition of 30 wt.% of TEPA on mesoporous silica nanotube (EMSNT) increased the adsorption of CO_2, due to low viscosity of TEPA, high content of amine, and increased active sites for CO_2 adsorption. The maximum CO_2 adsorption capacity was achieved at 9.31 mmol/g under the experimental conditions of 20°C and 8.8 atm. The adsorbent also exhibited good thermal stability and reusability within 12 cycles of adsorption-desorption process. Therefore, the combination of two functional materials may enhance the effectiveness of CO_2 adsorption performance. In another study, Taheri and co-workers [18] studied about functionalization of PEI on HNTs adsorbent for the CO_2 adsorption. The modified HNTs showed an increased number of surface area and pore volume, thus provides higher availability and dispersion of PEI on support, as well as increasing CO_2 adsorption sites. Zhang et al. [19] studied the effect of surfactant on SBA-15 and modification with amine towards CO_2 adsorption. They indicated that the existence of P123 on SBA-15, compared to the calcined SBA-15, has developed good synergistic effect between P123 and TEPA, thus enhances the adsorbent stability. As aforementioned, an excessive amount of TEPA may contribute to pore blockage and worsen the effect of pore mouth by blocking the amine active site on the inner pore. The optimum amount of amine obtained in this study was 60 wt.% for the CO_2 adsorption. Yusof et al. [20] examined the effect of metal oxide on fibrous silica (FS) for CO_2 physisorption and chemisorption. They reported that the high surface area and porosity enhanced the dispersion of metal oxide, together with an increase of the accessibility of CO_2. Besides, they also found that the ultrasound assisted impregnation method increased the dispersion of metal oxide and developed the basic active sites for CO_2 adsorption. Figure 1 illustrates the capability of CaO loaded FS as the best adsorbent for CO_2 physisorption (0.76 mmol/g) and high stability after tested for 5 cycles. Chanapattharapol et al. [21] investigated the effect of FeO on MCM-41 towards CO_2 adsorption. They found that the addition of 0.5 wt.% of FeO increased the surface area from 1530 m^2/g to 1548 m^2/g. They conclude that surface area is one of the main factors that influences CO_2 adsorption, apart from the presence of d orbitals from Fe and π bonding on CO_2 for electron transfer. In conclusion, the CO_2 adsorption performance greatly depends on the synergistic effect between the supporting material and the additive. To achieve an optimum synergistic effect, high dispersion of additive on the support may lead to the high number of active sites, thus increasing the interactions with CO_2 and contributed to superior CO_2 adsorption.

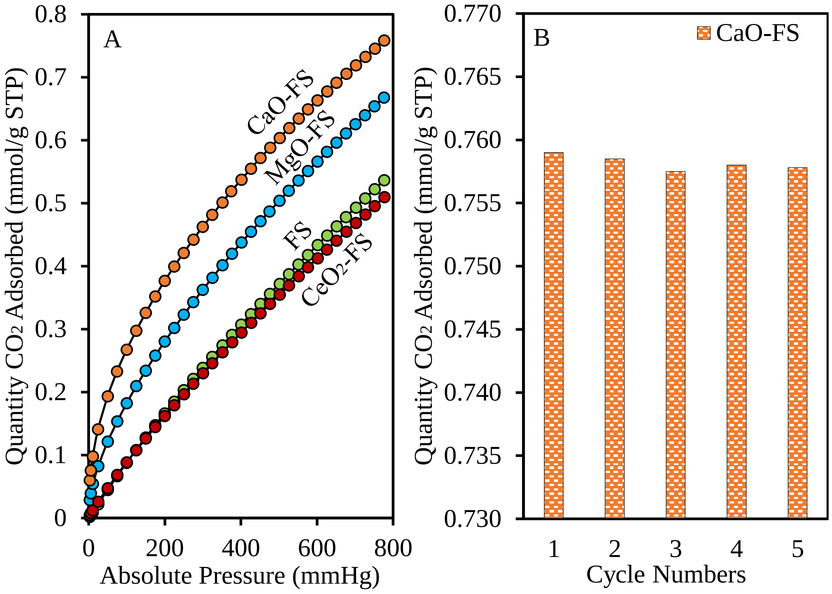

Figure 1. (A) CO_2 adsorption isotherms of FS, CaO-FS, MgO-FS, and CeO_2-FS. (B) Reusability of CaO-FS on CO_2 adsorption. (Reproduced from Figure 9 of Ref. [20] with copyright permission from Elsevier).

Table 2. Physicochemical properties and CO_2 adsorption of silica-based adsorbent.

Adsorbent	Additive		BET Surface Area (m^2/ g)	Total Pore Volume (cm^3/g)	Temp. (°C)	CO_2 Adsorption Capacity (mmol/g)	Ref.
	Type	Wt%					
EMSNT	TEPA	30	382	0.620	20	9.31	[17]
IMSiNT	PEI	30	341	0.499	20	7.84	[18]
SBA-15	TEPA	60	2.2	0.007	75	5.39	[19]
FS	CaO	5	45	0.098	25	0.76	[20]
MCM-41	FeO	0.5	1548	1.360	25	0.87	[21]

Carbon-Based Adsorbents

Carbon-based adsorbent is widely used materials that offers low cost, abundant sources, and highly efficient material for CO_2 adsorption. Wei et al. [22] studied bagasse sugar cane derived activated carbon (KAC) by reactivation of $ZnCl_2$-KOH and modification with tetraethylenepentamine (TEPA) (5–50 wt.%) to increase the adsorption performance of CO_2 (15% CO_2/85% N_2). It is noteworthy that the increasing of TEPA from 5 to 50 wt.% resulted in the decreasing of CO_2 adsorption capacity due to micropores blockage on KAC. Therefore, 5 wt.% of TEPA showed the best CO_2 adsorption at 3.62 mmol/g. Keller et al. [23] prepared hollow fiber CNT and modified with different wt.% loading of polyethylenimine (PEI). The result showed 20 wt.% of PEI on CNT presented the optimum CO_2 adsorption capacity (2.12 mmol/g). The increase of amine additive boosted the chemisorption capacity, but the uncontrolled addition may decrease the surface area and pore volume, and affected the CO_2 physisorption performance. Guo et al. [24] studied the effect of different supports for MgO modification towards CO_2 capture. They found that rice husk (RHA) impregnated MgO (20 wt.%) achieved the optimum CO_2 adsorption at 4.56 mmol/g due to the highly dispersed MgO nano particles that leads to the higher amount of basic active sites formation. Moreover, the adsorbent displayed good stability after reused for 10 cycles and indicated high potential in CO_2 adsorption on flue gases. Boruban and Esenturk [25] agreed with the finding of Guo et al. [24], in which the addition of metal oxide was capable of enhancing the CO_2 adsorption efficiency. Heo and Park [26] found that the CO_2 adsorption performance is also affected by the pore structure of additive for higher affinity of CO_2 and not limited to the surface area. In summary, carbon-based material offers a great potential as CO_2 adsorbent by virtue of relatively inexpensive and abundance supply in the economical perspectives. However, the appropriate modification method and suitable additive loading are vital to develop an excellent bifunctional carbon-based CO_2 adsorbent.

Table 3. Physicochemical properties and CO_2 adsorption of carbon-based adsorbent.

Adsorbent	Additive		BET Surface Area, (m^2/ g)	Total Pore Volume, (cm^3/g)	Temp., (°C)	CO_2 Adsorption Capacity, (mmol/g)	Ref.
	Type	wt.%					
KAC	TEPA	5.0	1832.0	1.190	60	3.62	[22]
CNT	PEI	20.0	34.7	0.234	25	2.12	[23]
RHA	MgO	20.0	39.0	0.120	200	4.56	[24]
AC	CuO	13.7	835.0	0.417	79 – 230	0.60	[25]
MCs	MgO	4.6	228.0	0.107	40	1.22	[26]

CONCLUSION

In this review, we focus on the bifunctional materials (BFMs) for CO_2 adsorption performance. Three types of adsorbents were discussed: zeolite-based, silica-based, and carbon-based materials on account of their high surface area, high porosity, tuneable pore structure, and high stability for regeneration purpose. We conclude that the synergistic relationship between support and additives (amine and metal oxide) may develop an excellent BFMs toward CO_2 adsorption. The role of support with high surface area and porosity provides high accessibility of additives, thus increasing the affinity and stability of the adsorbent towards CO_2 adsorption. BFMs show excellent potential as CO_2 adsorbent with widely tuneable properties. With the increasing demands for CO_2 capture approach, synergistic development of efficient BFMs presents an exciting perspective. The appropriate synthesis strategies and additives (type and loading amount) are prerequisite for the excellent design of CO_2 adsorbent. Besides, a comprehensive investigation is needed to provide an in depth and extensive understanding of the CO_2 capturing process via the study of the CO_2-material interaction.

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