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CO_2 Adsorption By Various Catalysts

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ABSTRACT

Global warming arising from the emission of greenhouse gases, especially CO_2, has become a biggest issue all over the world in the recent years. Though various CO_2 capture technologies have been proposed, chemical absorption and adsorption are currently believed to be the most suitable ones for post-combustion power plants. In this review paper, we will discuss different physical adsorbents; various mesoporous solid adsorbents impregnated with polyamines and grafted with amines are reviewed. The major concern is for CO_2 adsorption capacity at different temperature and pressure are compared and discussed. More effective and less energy-consuming regeneration techniques for CO_2-loaded adsorbents are also proposed.

Keywords: CO_2 capture technology, adsorbents, micro or mesoporous materials, post-combustion

1. INTRODUCTION

It can be understood that to develop an appropriate CO_2 capture adsorbent should satisfy (1) low-cost raw materials, (2) low heat capacity, (3) fast kinetics, (4) high CO_2 adsorption capacity, (5) high CO_2 selectivity and (6) thermal, chemical and mechanical stabilities under extensive cycling. A variety of solid adsorbents have been proposed to take into account of their structures and compositions, adsorption mechanisms, and regeneration. In this article, physical adsorption, mesoporous adsorbents impregnated and grated with amines, grafting using supercritical fluid (SCF), and regeneration techniques are reviewed.

1.1. Zeolites

Zeolitic adsorbents have played a major role in the development of adsorption technology. Zeolites are porous crystalline alumina silicates. The zeolite framework consists of an assemblage of SiO_4 and AlO_4 tetrahedral, joined together in various regular arrangements through shared oxygen atoms to form an open crystal lattice containing pores of molecular dimensions into which molecules can penetrate. Table 1 shows the CO_2 adsorption properties of different zeolites and zeolite-like materials. As seen, the adsorption capacity decreased drastically when the temperature increased from 298 to 323 K. In terms of CO_2 adsorption kinetics, zeolites are ranked among the fastest adsorbents, reaching equilibrium capacity within minutes. Moreover, a large number of studies were done on NaX faujasite using different recycling configurations, including temperature swing and pressure swing adsorption. Zeolites generally operate without any loss in performance, provided that the feed stream is strictly dry. Although low silica materials exhibit high adsorption capacity and selectivity at low pressure with favourable isotherms, they are very sensitive to the presence of water, which strongly inhibits the adsorption of CO_2.The CO_2 adsorption capacity on SAPO is lower than X and Y faujasites [1]. At 288 K and 100 kPa, the T-type zeolite nanoparticles showed 4.01 mmol/g CO_2 adsorption capacities, 30% higher than micro-level T-type zeolite. The synthesized T-type zeolite nanoparticles have promising adsorption capability and recyclability for the separation of CO_2/N_2 and CO_2/CH_4 in the potential application to post-combustion CO_2 separation or natural gas purification process [2].

In deduction, because of their often highly favourable CO_2 adsorption isotherms, zeolites and zeolite-like materials with low Si/Al ratios are among the most promising adsorbents for CO_2 capture from flue gas. However, because of their highly hydrophilic character, the flue gas needs extensive drying prior to CO_2 capture. Notice that among zeolites, 13X is has been the most investigated material for the purpose of CO_2 capture [1].

Table 1: Literature on CO_2 adsorption capacity by zeolites.

Name of zeolites	CO_2 adsorption temperature (K)	Pressure	CO_2 adsorption capacity	Year	References
NaX/1	298	0.1-0.4 bar	2.8-3.9	2004	[6]
NaX/1	323	0.1-0.4 bar	1.43-2.49	2004	[6]
LiX/1	303	0.1-0.4bar	3.1-4.6	2006	[4]
NaY/2.4	323	0.1-0.4bar	0.45-1.17	2007	[7]
CsY/2.4	333	0.1-0.4bar	0.86-1.2	2010	[5]
KY/2.4	333	0.1-0.4bar	0.75-1.6	2010	[5]
Silicalite/ •	334	0.1-0.4bar	0.16-0.45	1996	[8]
H-ZSM-5/30	313	0.1-0.4bar	0.7-1.5	2002	[9]
Li-MCM-22/15	333	0.1-0.4bar	0.68-1	2009	[10]
Zeolite 13X	295	100KPa	4.50	2004	[11]
Zeolite 13X	298	1000KPa	6.52	2004	[12]
NaX	298	100KPa	4.98	2006	[19]
NaY	295	100KPa	4.00	1995	[11,13,14]
Zeolite 5A	298	100KPa	4.73	2010	[18]
ZSM-5	313	100KPa	2.59	2004	[11,15]
Chabazite	304	100KPa	3.27	2012	[16]
Chabazite	304	1200KPa	4.32	2012	[16]
H-SSZ-13	298	100KPa	3.98	2012	[17]
Beta	303	100KPa	1.75	2009	[15]
Beta	308	1100KPa	3.27	2010	[20]
T-type	288	100KPa	4.81	2013	[2]
T-type	298	100KPa	3.94	2013	[2]
Zeolite NaKA	273	101KPa	3.36	2013	[21]

1.2. CARBON

Activated carbons are used because of their wide availability, low cost and high thermal stability. It is largely established that activated carbons have advantages over other CO_2 adsorbents. Among the carbon based adsorbents reported in the literature, activated carbons (ACs) and carbon nanotubes (CNTs) are the most investigated materials. CO_2 adsorption on activated carbons has been studied experimentally and theoretically for a long time and has found commercial applications. There is a wide range of activated carbons with a large variety of microporous and mesoporous structures. Activated carbon may be produced from many raw materials such as coal, coke pitch, wood or biomass sources (e.g., saw dust, coconut shells, olive stones), often via two steps: carbonization and activation. Carbon molecular sieves (CMS), which are a sub-class of activated carbon with narrow pore size distribution (PSD), are kinetic-based adsorbents. They have been commercialized mainly for the separation of air and the production of high purity N_2. However, at low CO_2 partial pressure, activated carbons exhibit lower adsorption capacity and selectivity than zeolites due mainly to their less favourable adsorption isotherms. In spite of the hydrophobic character of carbon-based adsorbents, their CO_2 adsorption ability is adversely affected by the presence of water vapour[1].

The physically activated carbons (PAC) exhibited a large adsorption of CO_2 of 1.45 mmol/g at a small partial pressure of CO_2 (10 KPa and a temperature of 0^0C). These PACs were prepared by activation in a stream of CO_2 and had significant amounts of ultra micropores, which were established by analysing the adsorption of CO_2 with a density functional theory. The uptake at such low pressures of CO_2 is of most importance for an adsorption-driven CO_2 capture from flue gas at large power stations, as it is difficult to imagine a pressurization of the flue gas. Activated carbons are attractive sorbents as they have high capacities for adsorption of CO_2, are tolerant to water in the flue gas, and can operate under either kinetic or equilibrium conditions[3].

Table 2: Literature on CO_2 adsorption capacity by Activated Carbon

Name Carbon Material	Temperature (K)	Pressure	Adsorption Capacity of CO_2 (mmol/g)	Year	References
AC	298	0.1-0.4bar	0.6-1.5	2001	[22]
AC	328	0.1-0.4bar	0.25-0.8	2001	[22]
SWCNT	308	0.1-0.4bar	0.5-1.25	2003	[23]
MWCNT	333	0.1-0.4bar	0.34-0.9	2009	[24]
Mesoporous Carbon	298	100KPa	1.5	2010	[26,27]
Mesoporous Carbon	298	1000KPa	3.0	2011	[26,27]
Activated Carbon	298	100KPa	2.27	2010	[25]
Activated Carbon	298	3000KPa	21.29	2010	[25]
Microporous Carbon	298	100KPa	4.0	2012	[28]
PAC(grass utility)	273	10KPa	1.45	2013	[3]
PAC(horse manure)	273	10KPa	1.36	2013	[3]
PAC(beer waste)	273	10KPa	1.31	2013	[3]

1.3.MOFs and zeolite-like MOFs

Last 20 years have seen a remarkable progress in the design, synthesis, and characterization of metal–organic frameworks (MOFs) owing to their various structural and chemical diversity and their potential applications in gas storage, ion exchange, molecular separation, and heterogeneous catalysis. These micro porous crystalline solids are composed of organic bridging ligands or “struts” coordinated to metal-based nodes to form a three-dimensional extended network with uniform pore diameters typically in the range 3 to 20. In summary, MOFs, ZMOFs and COFs may be promising materials for CO_2 removal provided that more favourable CO_2 adsorption isotherms are obtained. Their selectivity and capacity at low partial pressure of CO_2 in gas mixtures are quite low and more likely to be suitable for CO_2 storage rather than CO_2 separation from flue gas. Although in their early stages of development, MOFs, ZMOFs and COFs are promising materials for CO_2 adsorption showing very interesting and adjustable properties[1].

Table 3: Literature on CO_2 adsorption capacity by MOF & Z-MOF.

Name of MOF & Z-MOF	Temperature (K)	Pressure	Adsorption Capacity of CO_2	Year	References
MOF-508	323	0.1-0.4bar	0.1-0.7	2008	[34]
Cu-BTC	298	0.1-0.4bar	0.5-2	2007	[35]
MIL-53	303	0.1-0.4bar	0.5-1.15	2009	[29]
Ni/DOBDC	296	0.1-0.4bar	2.7-4.01	2008	[32,33]
Co/DOBDC	296	0.1-0.4bar	2.8-5.36	2008	[32,33]
Mg/DOBDC	296	0.1-0.4bar	5.36-6.8	2009	[30,32]
ZIF-78	298	0.1-0.4bar	0.77-1.36	2010	[31,36]
MOF-177	298	100KPa	1.73	2010	[18]
MOF-177	298	1400KPa	9.02	2010	[18]
CD-MOF-2	298	100KPa	2.68	2011	[37]
MOF-74	298	110KPa	4.86	2005	[38]
MOF-177	298	4250KPa	33.93	2005	[38]

1.4. Amine-functionalized adsorbents

The technology currently used in industry for CO_2 capture is absorption with liquid amine solutions. The removal of CO_2 by amines occurs via the widely accepted formation of carbamate and bicarbonate species. These are reversible reactions that permit the regeneration of amines, typically by heating the CO_2-rich solution.

The liquid amine absorption process inspired researchers to use amine-modified solid materials as adsorbents for CO_2 capture. As far as flue gas treatment is concerned, it was anticipated that supported amines will maintain a high selectivity toward CO_2 with a negligible uptake of other components, particularly N_2. Although the early efforts to produce amine functionalized adsorbents were not particularly successful in terms of adsorption capacity, but it is the increasing interest in the subject matter.

We have broadly organized the present section according to the type of interactions between amine groups and the support, namely (i) amine-impregnated materials where mostly weak interactions occur, and (ii) covalently bonded amine-containing species, obtained typically via surface-grafting of amino silanes. The rationale behind such classification is that materials with either strong or weak interactions exhibit a number of common characteristics. An example is that grafted materials offer comparatively higher rate of adsorption than amine-impregnated adsorbents and, in some cases even higher than commercial adsorbents such as 13X. However, the organic content of amine-grafted adsorbents depends on the surface density of hydroxyl groups, needed to anchor the aminosilane. As for impregnated amines, higher loadings may be achieved, but often accompanied by increasingly strong diffusion limitations [1].

Table 4: Literature data on CO2 adsorption capacity of amine-impregnated adsorbents

Support	Amine & Amine loading	Temperature	Adsorption Capacity	Year	References
MCM-41	PEI(50%)	75 ºC	2.1	2002	[39]
MCM-41	PEI(50%)	75 ºC	2.84	2005	[40]
SBA-15	PEI(50%)	75 ºC	3.18	2009	[41]
KIT-6	PEI(50%)	75 ºC	1.95	2008	[42]
MONOLITH	PEI(65%)	75 ºC	3.75	2009	[43]
As-synthesized SBA-15	TEPA(50%)	75 ºC	3.25	2006	[44]
As-synthesized MCM-41	TEPA(50%)	75 ºC	4.54	2008	[45]
As-synthesized SBA-15	TEPA+DEA (50%)	75 ºC	3.77	2008	[46]
PE-MCM-41	DEA(76%)	25 ºC	3	2005	[47]
Mesoporous Al2O3	DETA(40%)	57 ºC	1.4	2008	[48]
Mesoporous SiO2	PEI(40%)	70 ºC	2.4	2008	[48]
SBA-15	PEI(50%)	75 ºC	1.36	2009	[49]
PMMA	TEPA(41%)	70 ºC	13.88	2008	[52]
PMMA	Ethyleneamine+acrylonitrile	25 ºC	4.18	2005	[53]
PMMA	DBU(30%)	65 ºC	2.34	2008	[56]
PMMA(Diaion)	PEI(40%)	40 ºC	3.60	2009	[54]
AOS Carbon	PEI(5%)	25 ºC	1.98	2009	[55]
13X	MEA(25%)	75 ºC	0.45	2007	[50]
Beta-zeolite	TEPA(38%)	30 ºC	2.08	2009	[51]
TiNT	Tetraethylene pentamine	303K	4.37	2013	[57]

Table 5: Literature data on CO_2 adsorption capacity of amine-grafted adsorbents

Support	Amine & Amine loading(mmol/g)	Temperature (°C)	Adsorption Capacity(mmol/g)	Year	References
Silica Gel	AP(1.26)	50	0.89	1995	[58]
MCM-48	AP(2.3)	25	2.3	2003	[59]
HMS	AP(2.29)	20	1.59	2005	[60]
HMS	TRI(4.57)	20	1.34	2006	[61]
PE-MCM-41	TRI(7.9)	50	1.59	2010	[62]
SBA-15	TRI(5.8)	60	1.80	2005	[63]
MS	TRI(5.18)	25	1.74	2008	[64]
SBA-16	EDA(0.76)	27	1.4	2007	[65]
SBA-15	AP(2.56)	65	0.45	2007	[66]
SBA-16	EDA(3.06)	60	0.727	2008	[67]
SBA-15	AP(2.72)	25	1.54	2008	[68]
SBA-12	AP(2.13)	25	1.04	2008	[69]
MS	AP(1.6)	30	0.24	2009	[70]
MSP	EDA(0.99)	60	0.73	2009	[71]
MCM-48	TREN(4)	50	1.36	2010	[72]
ITQ-6	AP(1.26)	20	0.67	2009	[73]
SBA-15	Amine-dendrimers(1.25)	20	1	2008	[74]
SBA-15	Azridine polymer(9.78)	75	4	2009	[75]

2. Conclusion

New techniques have been achieved towards the development of a CO_2 capture technology based on adsorption. Physical adsorbents such as zeolites, carbon-based materials and MOFs were found to be suitable, mostly at low temperature and high pressure. These adsorbents, however, often adsorb water vapor preferentially over CO_2, and their CO_2 adsorption capacity at low pressure is not sufficiently high. Although these materials may provide elegant solutions for CO_2 sequestration and storage, they are not particularly suitable for post-combustion gas treatment. The strategies being used include surface modification to enhance the interactions with CO_2, thus increasing the adsorption capacity at low pressure.

Another route is to design completely new materials such as ZMOFs and COFs with increased tolerance to moisture in the gas feed, thus improved CO_2 selectivity. Likewise, tremendous progress has been achieved in the development of novel chemical adsorbents such as amine-modified materials with large surface area. By optimizing the synthesis conditions and using supports with adequate structural properties, it was possible to develop materials with superior CO_2 adsorptive properties, particularly suitable for flue gas treatment. Typically, these materials exhibit large CO_2 adsorption capacity even at low pressure, high rate of adsorption and desorption, and excellent tolerance to moisture in the feed. Furthermore, contrary to physical adsorbents, the selectivity of amine-functionalized materials is not significantly affected by temperature, at least within the range of interest for flue gas treatment. While the stability of this kind of adsorbents has been questioned, it was recently demonstrated that their stability may be dramatically enhanced during thousands of adsorption –desorption cycles, provided that the feed and purge gases contains moisture. The role of moisture is to prevent the formation of urea linkages, which is the main source of material deactivation.

In this review, it is clearly stated that a steady improvement in the CO_2 adsorptive properties at different temperature and pressure. The course followed so far has resulted in major achievements that may well pave the way for an alternative CO_2 capture technology in the near future.s

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