

# A REVIEW ON CO<sub>2</sub> SORBENTS

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**Abstract:** Fossil fuels are the major energy source used in the world and will continue to dominate in the future. For the coal-dependent countries, the key to the emission reduction of CO<sub>2</sub> will be the capture of CO<sub>2</sub> in coal-fired power plants. Currently available CO<sub>2</sub> sorbents are reviewed in this paper. Based on the principles of various separation technologies, absorption and adsorption are discussed accordingly. In terms of the application temperature, absorption materials are categorized into high-temperature absorbent and low-temperature absorbent and their latest progress are included. For the adsorption, different materials such as activated carbon, zeolite and MOFs and etc. are discussed thoroughly. At the end, the future trend of CO<sub>2</sub> separation is proposed. It is suggested that since any single method cannot meet the requirements of coal-fired power plants, feasible approach for CO<sub>2</sub> separation will be to combine the advantages of all the available methods, for example, adsorbents impregnated with amines, porous polymer impregnated with organic solvents and new structured adsorbents such as ionic liquids and metal organic frames.

## 1. INTRODUCTION

Global climate change due to green house effect is drawing attentions world widely. Carbon dioxide is the largest contributor in regard of its amount present in the atmosphere, contributing to 60% of global warming effects. The total amount of CO<sub>2</sub> emitted in the world reaches 20 billion annually, among which 75% is from the burning of fossil fuels. Since emissions from coal-fired power plants contribute 40.6% of the total emissions, the key to the CO<sub>2</sub> emission reduction is to reduce the emissions from coal-fired power plants.

In all routes to reduce the emission of CO<sub>2</sub> to the atmosphere, whether to convert to chemical raw materials or to sequester in deep sea, the separation and capture of CO<sub>2</sub> is the key step. The technologies to capture CO<sub>2</sub> in coal-fired power plants include pre-combustion capture, post-combustion capture and oxy combustion. The pre-combustion capture, complicated and costly, is suitable for

newly-built power plants; Oxy combustion is not a mature technique, and the operation/maintenance fee is very high; Post-combustion capture, which is to separate CO<sub>2</sub> from flue gases, mature and suitable for the retrofit of existing power plants, will be the key method to reduce the emission of CO<sub>2</sub> in coal-fired power plants.

Flue gases from coal-fired power plant has characteristics of high flux (a typical 300 MW unit emits about 12 million per hour), high flow speed, high temperature (about 130 °C after the electrostatic precipitator), relatively low volume fraction of CO<sub>2</sub> (12%~15%), mixed complex gases (containing particulates, SO<sub>2</sub>, NO<sub>x</sub>, and HCl), and etc., thus separation of CO<sub>2</sub> in the flue gas is very challenging. Currently, the methods used to separate and capture CO<sub>2</sub> include absorption, adsorption, membrane separation, cryogenic separation and biological methods. Absorption and adsorption will be reviewed here.

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## 2. ABSORPTION

### 2.1. Low temperature absorbents

The basic principle of solvent absorption is using alkaline solutions to capture acidic CO<sub>2</sub> in the absorber and then accomplishing the separation of CO<sub>2</sub> and the regeneration of the solvents through desorption. Currently available solvents include alkanolamine (such as monoethanol amine (MEA), diethanolamine (DEA), 2-(2-Aminoethoxy) ethanol (DGA), methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP) and etc.), and ammonia, which hold the advantages of high absorption rate, wide-ranged CO<sub>2</sub> concentration and technical maturity. However, organic solvents is corrosive to the equipments, easily foamy, easy to react with other acidic gases such as SO<sub>2</sub>, NO<sub>2</sub> irreversibly, and has the disadvantages of high regeneration energy consumption and escaping problem of ammonia. In addition, these solvents require an operating temperature lower than 100 °C, thus it is necessary to decrease the flue gas temperature (above 600 °C after low temperature superheater, circa 140 °C after economizer and air-preheater.), which increases the energy consumption of electricity generation.

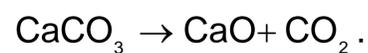
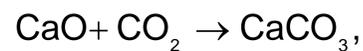
Ionic liquids (ILs), composed of organic cations and inorganic anions, are salts in liquid state at room temperature. CO<sub>2</sub> can interact strongly with ILs and has a very high solubility in them. Typical ILs applied to CO<sub>2</sub> absorption include imidazolium-based ionic liquids, guanidinium ionic liquids and amino acid ionic liquids. Through amination and polymerization, the absorption of CO<sub>2</sub> in ILs can be improved. Advantages of using ILs are as following: no volatile substances are produced during the absorption of CO<sub>2</sub> in ILs; almost no loss of ILs is found during the cyclic reactions; a high absorption efficiency can be achieved; the energy consumption can be reduced from 30% to 16% [1] in comparison with alkanolamine solvents. The limitation of ILs is the high viscosity which will affect the mass transfer. liquidimidazolium-based ionic liquidsimidazolium-based

Enzyme to promote the absorption of CO<sub>2</sub> in K<sub>2</sub>CO<sub>3</sub> solution has been studied recently [2]. It was found that in K<sub>2</sub>CO<sub>3</sub>/KHCO<sub>3</sub> solution at 50 °C, the activity of carbonic anhydrase (CA) enzyme immobilized onto dense SiO<sub>2</sub>-ZrO<sub>2</sub> and SiO<sub>2</sub> nanoparticles can be maintained at 56-88%, compared with a 30% activity retention for their free CA enzyme counterpart.

### 2.2. High temperature absorbents

Carbon dioxide is acidic gas, easy to adsorb onto surfaces of alkaline oxides, such as Al<sub>2</sub>O<sub>3</sub>, MgO,

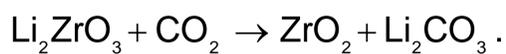
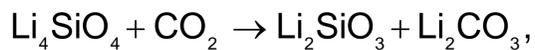
CaO, ZrO<sub>2</sub>, Li<sub>2</sub>O, and etc. These absorbents have good absorption ability and the products are carbonates which can decompose into metal oxides and CO<sub>2</sub> at high temperatures. Therefore, it accomplishes a close loop of CO<sub>2</sub> capture and cyclic utilization of absorbents. Taking CaO as an example, the reaction between metal oxides and CO<sub>2</sub> as follows:



The theoretical absorption capacity of CaO can reach as high as 78.6% and it also has a good wear resistance. But during the high temperature (550-700 °C) absorption, a thin layer of CaCO<sub>3</sub> formed on the surfaces of CaO particles would block the micropores and cause that CO<sub>2</sub> is difficult to diffuse into CaO particles to make direct contact, therefore lower the efficiency of the absorbent. On the top of that, the high temperature (800-900 °C) decomposition would lead to a further sintering of CaO particles, which decreases surface area and porosity, hence lowers the conversion efficiency of absorbents. Aimed to solve the abovementioned problems, many researchers have used zirconium, potassium, silicon to tune calcium-based absorbents to improve the cyclic conversion rate. At the same time, some tried to modify the structure. For example, Barker [3] found that the absorption capacity was only 8% after 25 cycles when using CaO with a diameter of about 10 μm to absorb CO<sub>2</sub>. They concluded that it was that the 22 nm thick layer of CaCO<sub>3</sub> prevented the further reaction between CaO and CO<sub>2</sub> and proposed that an ideal conversion rate can be achieved if CaO with a diameter less than 22 nm was used. Li et al. [4] used a material inert to CO<sub>2</sub> as a support to the porous structure, and the resulting CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> showed high porosity, high surface area and good resistance to sintering. The absorption ability was still maintained above 40% even after 50 cycles. Yi et al. [5] found that the existence of oxygen vacancy is favorable to the diffusion of CO<sub>2</sub>. Calcium-based absorbents doped with attapulgite were also studied and the absorption ability of the doped ones was improved 1.28 times compared to the undoped ones during the first 20 cycles [6].

Future researches on calcium-based absorbents will focus on improving the reactivity of CaO, methods can be adopted including [7,8]: (1) using steam treatment to increase surface area and porosity; (2) doping with other atoms; (3) pre thermal treatment; (4) use of nano materials; (5) use of porous inert materials as support; (6) composite materials.

Lithium-based materials such as  $\text{Li}_4\text{SiO}_4$  and  $\text{Li}_2\text{ZrO}_3$  are another type of high temperature absorbents under intensive researches. The reaction between these absorbents and  $\text{CO}_2$  is reversible, as following:



The performance of these absorbents varies with the synthesis methods used. Current researches focus on using different synthesis methods (for example solid state method and sol-gel method) and doping with metal elements (for example, Na, K, Mg, Ti) to modify lithium based absorbents. The absorption rate of  $\text{Li}_4\text{SiO}_4$  is greater but the absorption capacity per unit of mass is lower, thus a large amount of absorbents is required; compared to  $\text{Li}_4\text{SiO}_4$ , the absorption rate of  $\text{Li}_2\text{ZrO}_3$  is lower, it requires a higher synthesis temperature and longer synthesis hours.  $\text{LiCuO}_2$  absorption for  $\text{CO}_2$  is also reversible and its theoretical absorption capacity is the greatest in comparison with  $\text{Li}_4\text{SiO}_4$  and  $\text{Li}_2\text{ZrO}_3$ , can reach 40.1%, which makes  $\text{LiCuO}_2$  a potential high temperature absorbent.

### 3. ADSORPTION

The principle of adsorption is to separate and capture  $\text{CO}_2$  from gas mixtures by using solid adsorbents to adsorb  $\text{CO}_2$  selectively and reversibly. Adsorption is based on molecular attraction forces between the active sites on the surface of the porous solid adsorbents and the guest molecules, thus a highly active porous adsorption material is the core of adsorption. A highly active adsorption material should have abundant micropores, which is favorable to the adsorption of  $\text{CO}_2$  with a dynamic molecular diameter of 0.33 nm, and are also provided with a hierarchical porous structure with micropores, mesopores and macropores in series connection, which helps the diffusion of  $\text{CO}_2$ . Commonly used adsorbents include porous carbons, zeolites, silica-based mesoporous materials, metal-organic frameworks (MOFs), porous polymer materials (crystallized, amorphous) and hydrotalcite-like compounds.

#### 3.1. Porous carbons

Porous carbons, which have high surface areas, large pore volume, excellent chemical and thermal stability, are provided with great adsorption capability. The specific surface area of activated carbon is

normally in the range of 400~1000  $\text{m}^2/\text{g}$ , among which the micropores surface area account for above 95%. Activated carbon can be derived from various sources, such as anthracite, weakly caking coal, lignite, almond shells and etc. They are cheap and can satisfy the requirements of industrialization. But the adsorption capacity of porous carbons derived from different sources varies greatly and it depends strongly on the pore size and pore distribution. Currently studied activated carbons include wood-based powdery activated carbon (at 25 °C under  $3.5 \times 10^6$  Pa, the adsorption capacity reaches 25 mmol/g), coal-based granular activated carbon (the adsorption capacity is only 7 mmol/g) [9], petroleum pitch-based activated carbon (the adsorption capacity of the activated carbon prepared by chemical activation using KOH can reach 36 mmol/g at 25 °C under  $5 \times 10^6$  Pa) [10] and potato starch-based activated carbon. Activated carbons prepared from hydrothermally carbonized waste biomass achieved an adsorption capacity of 1.45 mmol/g at 0 °C under  $1 \times 10^4$  Pa [11]. Activated carbons showed very high adsorption capacity under high pressure, but their capacity was one order of magnitude lower under low  $\text{CO}_2$  partial pressure. Therefore, researches on activated carbons currently focus on how to improve their adsorption capability and separation selectivity under low  $\text{CO}_2$  partial pressure.

In the light of the above-mentioned disadvantages, incorporating nitrogen functional groups at high temperature and impregnating with amines were developed to modify the surface chemistry. Introducing nitrogen functional groups into the structure can improve its affinity to  $\text{CO}_2$ , increase the adsorption capacity and selectivity under low partial pressure. Pevida et al. [12,13] tried to incorporate nitrogen functional groups at high temperature and impregnate activated carbon with organic amine compounds [14,15] (diethylenetriamine (DETA), Pentaethylenhexamine (PEHA), Polyethylenimine (PEI)) to improve the surface chemistry. Incorporation of nitrogen functional groups can improve the adsorption capacity at ambient pressure to some degree, while the impregnation of amines needs to balance the ratio of amine density and porosity since the impregnated amines would lead to the blockage of the porous structure.

In addition, another efficient approach is to form different structures such as single-walled carbon nanotubes (CNTs), multi-walled CNTs and carbon molecular sieves. Although carbon nanotubes showed excellent adsorption performance, they are not suitable for high volume applications due to high cost.

### 3.2. Zeolites

Zeolites, occur naturally and can also be produced industrially on a large scale, are porous, aluminosilicate minerals with pore diameter in the range of 0.3-1.0 nm. Zeolites molecular sieves have advantages of large specific surface areas (~1000 m<sup>2</sup>/g), abundant micropores, uniform pore size distribution, pore size close to common molecules, highly polarized internal surface and strong electrostatic field, which make zeolites molecular sieves excellent adsorbents, showing a strong adsorption capability especially to small polarized molecules.

The inorganic and organic components of zeolites molecular sieves can be exchanged and the structure can be manipulated, therefore the adsorption and separation of CO<sub>2</sub> can be tuned by adjusting the functional groups. Many types of zeolites such as X, Y, A, β, ZSM, CHA, and etc. have been studied intensively. Siriwardane et al. [16] reported that the adsorption capacity of 13X and 4A is 3.64 and 3.07 mmol/g under the condition of 25 °C and 1x10<sup>5</sup> Pa CO<sub>2</sub> partial pressure. The cations in the zeolites structure are loosely held that can be exchanged by other ions such as alkali metals and alkaline-earth metals, by which the adsorption characteristics are manipulated. That the radius of metals can affect the adsorption capacity of zeolites was also observed. Impregnating or grafting zeolites with amines (for example, MEA) [17] could change the adsorption dramatically, which made physical adsorption transform into chemical adsorption with amino group as active centers. The adsorption capacity was increased and meanwhile the selectivity of CO<sub>2</sub> over CH<sub>4</sub> and N<sub>2</sub> was also enhanced greatly. Activated carbon honeycomb monolith-Zeolite 13X hybrid system could adsorb twice as much CO<sub>2</sub> as activated carbon honeycomb did alone [18]. High-throughput synthesis of several hundreds of zeolitic imidazolate frameworks (ZIFs) has been accomplished by Yaghi group [19] through the microreactions of either zinc(II)/cobalt(II) and imidazolate/imidazolate-type linkers. The resulting ZIFs possessed high porosity, and exhibited unusual selectivity for CO<sub>2</sub> capture from CO<sub>2</sub>/CO mixtures and extraordinary capacity for storing CO<sub>2</sub>: 1 liter of ZIF-69 could hold 83 liters of CO<sub>2</sub> at 0 °C, under ambient pressure. The same group [20] found that the adsorption capacity of CO<sub>2</sub> under low partial pressure was strongly dependent on the polarity of surface functional groups in ZIFs, ZIF-78 with a strong polar group of -NO<sub>2</sub> and ZIF-82 with a strong polar group of -CN exhibited a better selectivity than other ZIFs.

Ishibashi et al. [21] tested zeolites as adsorbents to separate CO<sub>2</sub> in a 1000 m<sup>3</sup>/h demonstration plant through pressure swing and temperature swing adsorption: the removal efficiency reached 90% and the reclaiming concentration was 99%; no adsorption efficiency drop was observed in a continuous operation of 2000 h; the adsorption temperature needed to be controlled at 50 °C since the adsorption capability decreased dramatically with increasing temperature and eventually disappeared above 200 °C. Another disadvantage of zeolites as adsorbents is strong hygroscopicity, thus not suitable in water containing environment.

### 3.3. Silica-based adsorbents

Mesoporous silica molecular sieves, which are prepared by using surfactants as templates through a series of processes like sol-gel and emulsification, are ordered mesoporous silica materials with well defined porous structure. Provided with high specific surface areas (>1000 m<sup>2</sup>/g), large pore volumes and continuously tunable pore sizes, mesoporous silica molecular sieves are under series of intensive researches. MCM-41 and SBA-15 were the most studied ones for CO<sub>2</sub> adsorption, and the research focus is to modify the surfaces using amine groups. The methods to introduce amine groups include impregnation, grafting or simple coating and filling pores and etc.

Mesoporous silica molecular sieves impregnated with amines for CO<sub>2</sub> separation were studied intensively. The pore size of MCM-41 molecular basket impregnated with PEI prepared by hydrothermal synthesis method is 2.8 nm. The adsorption capacity of MCM-41-PEI reached 3.02 mmol/g at 75 °C under ambient pressure when the loading of PEI was 75 wt.%. Different from conventional activated carbons and zeolites adsorbents, the adsorption capacity of MCM-41-PEI increased with temperature increasing [22]. A series of researches [23] have been carried out to test the stability and performance of MCM-41-PEI in simulated flue gas (14.9%CO<sub>2</sub>/4.25%O<sub>2</sub>/80.85%N<sub>2</sub>): the cyclic adsorption properties above 100 °C were not stable and the presence of water steam was good for the CO<sub>2</sub> adsorption when the content of water steam was lower than CO<sub>2</sub>. Franchi et al. [24] impregnated MCM-41 which has large pore size and volume with DEA, the resulting adsorbents exhibited better cyclic stability than zeolite 13X impregnated with DEA. Incorporation of ionic surfactants could improve the CO<sub>2</sub> adsorption capacity of MCM-41-TEPA, an adsorption capacity of 4.16 mmol/g was achieved for MCM-41

impregnated with 50 wt.% TEPA in 5% CO<sub>2</sub> atmosphere [25]. It has been reported that a larger amount of amino groups loading in the adsorbent resulted in the enhanced isosteric heat of adsorption, while AEAPS-functionalized MSU-H silica exhibited lower integrated isosteric heat of adsorption during the adsorption–desorption cycles than the other functionalized MSU-H silicas, which corresponded to less energy required to regenerate the adsorbent and made the regeneration of the adsorbent easier [26].

A series of mesoporous silica materials, MCM-41, MCM-48, SBA-15, SBA-16, and KIT-6, impregnated with 50 wt.% PEI have been investigated [27]. All PEI-loaded mesoporous silica exhibited faster adsorption kinetics, higher adsorption capacities and better stability than pure PEI. An adsorption capacity of 3.18 mmol/g at 75 °C under ambient pressure for SBA-15 adsorbents impregnated with 50 wt.% PEI was reported [28] and this value was 50% higher than previously reported.

Various organoamines (such as PEI, MEA, DEA, TEPA, PEHA, AMPD, and AEAE) supported by nanostructured silica were found to be regenerable and effective CO<sub>2</sub> absorbents at moderate temperatures from room temperature up to 100 °C [29]. The particle size of nanosilica was of advantage compared to other solid supports having similar or higher surface area but larger particle size. PEI and TEPA functionalized mesoporous silica capsules [30] showed an adsorption capacity of 6.6 mmol/g at 75 °C under 1x10<sup>5</sup> Pa CO<sub>2</sub> pressure and the adsorption capacity reached 7.9 mmol/g under simulated flue gas conditions (10% CO<sub>2</sub>). The CO<sub>2</sub> capture kinetics were found to be fast and reached 90% of the total capacity within the first few minutes. PEI impregnated adsorbents could be regenerated at 100 °C and exhibited good reversibility and stability during the first 50 cycles. As stated above, organoamines impregnated mesoporous silica exhibited good adsorption capacities, but the stability and desorption of these materials have yet to be tested in real flue gas, on the top of which, problems like slow desorption and amines leakages also need to be tackled.

Besides the impregnation of organoamines, grafting is another approach to modify mesoporous silica. Chaffee group successfully prepared a series of aminopropyl-functionalized hexagonal mesoporous silicas (HMS) [31], which have high surface areas, varying contents of aminopropyl groups, and can adsorb/desorb more CO<sub>2</sub> reversibly. HMS materials exhibited good adsorption kinetics and

could reach equilibrium in 4 minutes. A maximum adsorption capacity of 1.66 mmol/g was achieved in 20 °C, under the dry atmosphere of 90%CO<sub>2</sub>/10%Ar. The degree of surface functionalization was proved to be dependent on the morphology of mesoporous silica (such as available surfaces, shapes and volumes of pores), the diffusion of solvents and the concentration of hydroxyl. The presence of water could improve the adsorption capacity of AEAPTS functionalized SBA-15, while SO<sub>2</sub> would lead to the failure of APTES-SBA-15 [32].

### 3.4. Metal organic frameworks

Metal organic frameworks (MOFs) are compounds consisting of metal ions or clusters coordinated to often rigid organic molecules to form one-, two-, or three-dimensional structures that can be porous. The choice of metal and linker dictates the structure and hence properties of the MOFs, thus the tunable structure and properties drew more and more attentions in the adsorption application.

MOF-210, prepared by Yaghi group, has a surface area of 6240 m<sup>2</sup>/g, which is the highest reported for crystalline materials [33]. It exhibited an adsorption capacity of 2400 mg/g at room temperature and under 5x10<sup>6</sup> Pa pressure, which is also the highest reported so far. The CO<sub>2</sub> adsorption capability of MOFs in humid conditions has also been investigated. The adsorption capacity of Ni-MOF74 was 3.28 mmol/g at 25 °C, under 1x10<sup>4</sup> Pa CO<sub>2</sub> partial pressure, which was higher than zeolites under the same conditions, and even in humid conditions, Ni-MOF74 can still maintain a high CO<sub>2</sub> adsorption capacity. Zr-MOFs exhibited good stability and CO<sub>2</sub> adsorption capacity, and impurities like O<sub>2</sub> and SO<sub>2</sub> in flue gas have little effects on the selectivity of CO<sub>2</sub> [34].

The major disadvantage of MOFs is low adsorption capacity under ambient pressure, therefore many studies have been carried out to improve the selectivity and adsorption capacity of MOFs under ambient pressure by tuning metal ions and organic linkers. It seemed that creating open metal sites is an effective approach. The selectivity of Mg-MOF-74 with open magnesium sites was very high: it only adsorbed CO<sub>2</sub> in 20%CO<sub>2</sub>/CH<sub>4</sub> gas mixtures, and the dynamic adsorption capacity was the highest among porous materials [35]. Organoamines were also used to modify the adsorption performance of these materials. Ethylenediamine functionalized H<sub>3</sub>Cu<sub>4</sub>Cl<sub>3</sub>(BTTri)<sub>8</sub> exhibited a higher CO<sub>2</sub> uptake compared to non-grafted materials [36]. Functionalizing the well-known MIL-53(Al) metal-organic framework

with amino groups increased its selectivity in CO<sub>2</sub>/CH<sub>4</sub> separations by orders of magnitude while maintaining a very high capacity for CO<sub>2</sub> capture [37]. Some studies suggested water molecules occupying metal sites could improve CO<sub>2</sub> adsorption in metal organic frameworks [38]. Modification of MOFs by using mixed ligands could improve the selectivity of CO<sub>2</sub> over CH<sub>4</sub>, resulting Zn<sub>2</sub>(NDC)<sub>2</sub>(DPNI) [NDC=2, 6-naphthalenedicarboxylate, DPNI=N, N'-di-(4-pyridyl)-1,4,5,8-naphthalene tetracarboxydiimide] synthesized by micro-wave heating exhibited a selectivity of 30 for CO<sub>2</sub> over CH<sub>4</sub> [39]. In addition, introducing some polar groups such as -NH<sub>2</sub>, -SO<sub>3</sub>H and -COOH could also tune the surfaces of MOFs [40].

In summary, researches on MOFs are relatively new. Although MOFs exhibited very high adsorption capacity under high pressure, the adsorption capacity under low pressure is still low compared to other adsorbents. The future investigations will focus on the improvements of the stability, cyclic performance and competitive adsorption capacity under ambient conditions.

### 3.5. Other adsorbents

The abovementioned MOFs have loose coordinated bonds, leading to unstable structures of MOFs. By contrast, covalent organic frameworks (COFs) can hold abundant porous channels meanwhile still maintaining their stability. A series of crystallized porous COFs (COF-1, COF-5, COF-6, COF-8, COF-10, COF-12, COF-13) have been synthesized by Yaghi groups [41]. Comprised of 3D structure with 3D medium-sized pores, COF-102 and COF-103 exhibited high surface area of 3473 m<sup>2</sup>/g and 4210 m<sup>2</sup>/g and exceptional adsorption capacity. The adsorption capacity of COF-102 could reach 1180 mg/g at 25 °C under 3.5x10<sup>6</sup>Pa.

Apart from crystalline porous polymers, amorphous porous polymers are being investigated as adsorbents [42-44]. A series of porous polymer networks (PPNs) with exceptionally high surface area and gas-uptake capacities has been prepared, among which PPN-4 exhibited a high surface area of 6461 m<sup>2</sup>/g and a CO<sub>2</sub> adsorption capacity of 2121 mg/g at 22 °C under 5x10<sup>6</sup>Pa. Sulfonic acid and its lithium salt grafted PPNs exhibited better adsorption capacity and selectivity than non-grafted one. PPN-6-SO<sub>3</sub>Li showed a CO<sub>2</sub>-uptake capacity of 3.7 mmol/g which is higher than 1.2 mmol/g of non-grafted one, and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 414/1 [45,46]. Porous polymer networks show exceptionally good adsorption performance as described

above, but the fabrication procedures are very complex and costly, and on the top of which the powdery appearance raised a real problem in practical applications.

Attempts have been made to use hydrotalcite-like compounds with a general formula of [M<sub>1-x</sub><sup>2+</sup>M<sub>x</sub><sup>3+</sup>(OH)<sub>2</sub>][A<sup>n-</sup>]<sub>x/n</sub>·zH<sub>2</sub>O (M<sup>2+</sup> is Mg<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>; M<sup>3+</sup> is Al<sup>3+</sup>, Ga<sup>3+</sup>, Fe<sup>3+</sup>, Mn<sup>3+</sup>; A<sup>n-</sup> is CO<sub>3</sub><sup>2-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) for CO<sub>2</sub> adsorption, and these compounds possess high surface area and can adsorb acidic CO<sub>2</sub>. The current researches focused on Mg-Al-CO<sub>3</sub> compounds to have divalent Mg<sup>2+</sup> or CO<sub>3</sub><sup>2-</sup> substituted. Divalent ions substituted for Mg<sup>2+</sup> include Co<sup>2+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup> or the combinations of these ions and anions replacing for CO<sub>3</sub><sup>2-</sup> include Fe(CN)<sub>6</sub><sup>4-</sup>, Cl<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>. The adsorption capacity of K<sub>2</sub>CO<sub>3</sub>-doped Mg-Al-CO<sub>3</sub> increased from 0.47 mmol/g to 1.4 mmol/g if using Ga<sup>3+</sup> to substitute Al<sup>3+</sup> partially [47]. The major limitations of these materials are low capacity and as-yet-to-be tested cyclic performance.

Electrochemically promoted CO<sub>2</sub> adsorption on Pt coated K-βAl<sub>2</sub>O<sub>3</sub> exhibited a maximum adsorption capacity of 1130 mg CO<sub>2</sub>/g Pt and the adsorbent can be regenerated by electrochemical decomposition of previously stored compounds without increasing temperature [48]. It shows potential to be high temperature adsorbents.

## 4. CLOSING REMARKS

Based on the above analysis, it can be concluded that every available CO<sub>2</sub> capture technology has its own limitations: 1) Absorption methods requiring high generation energies, exhibiting low absorption capacities and causing corrosion to the equipments; 2) Solid adsorbents having low adsorption capacity and poor selectivity, limited to low temperatures application and delivering low-purity CO<sub>2</sub>.

Features of flue gases emitted from coal-fired power plants include complex compositions of SO<sub>x</sub>, NO<sub>x</sub>, and particulates, low CO<sub>2</sub> partial pressure (less than 15%), high temperature and high flux, which make flue gases very tricky to be tackled. Subsequently, it requires sorbents to have high capacity under low partial pressure, good selectivity, and stable physical/chemical properties to resist the interference of impurity gases. Currently, none of these methods reviewed previously can fulfill the challenges alone. The future trend of CO<sub>2</sub> capture will be to combine the advantages of all available technologies to produce composite sorbents with higher capacity, better selectivity and better cyclic performance. For example, using amines to functionalize the sorbents to achieve better selec-

tivity and capacity; adopting new-structured sorbents such as ionic liquids and MOFs. Flue gas in coal-fired power plants is at the range of 100-150 °C, none of the high temperature absorbents and low temperature adsorbent reviewed above can meet the requirements, thus it is necessary to develop new composite materials for CO<sub>2</sub> adsorption at this range.

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