



Review Paper

Functionalized Polymeric Membranes for CO₂ Capture

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- Microporous organic polymers (MOPs) for CO₂ capture
- Poly(ethylene oxide) and its cross-linked polymers, copolymers and polymer blend dense film membranes for CO₂ capture
- Facilitated transport membrane CO₂ capture

ABSTRACT

Reducing CO₂ emission and lowering the concentration of greenhouse gases in the atmosphere has quickly become one of the most urgent environmental issues. While a variety of technologies and methods have been developed, the separation of CO₂ from gas streams is still a critical issue. Apart from establishing new techniques, the exploration of membrane materials with high separation performance and low capital cost are of paramount importance. Functionalized polymers hold great potential as membrane materials in gas separation. In this paper, the research progress in functionalized polymers membrane materials for membrane-based high CO₂ permselectivities separations that are directly related to CO₂ capture were reviewed.

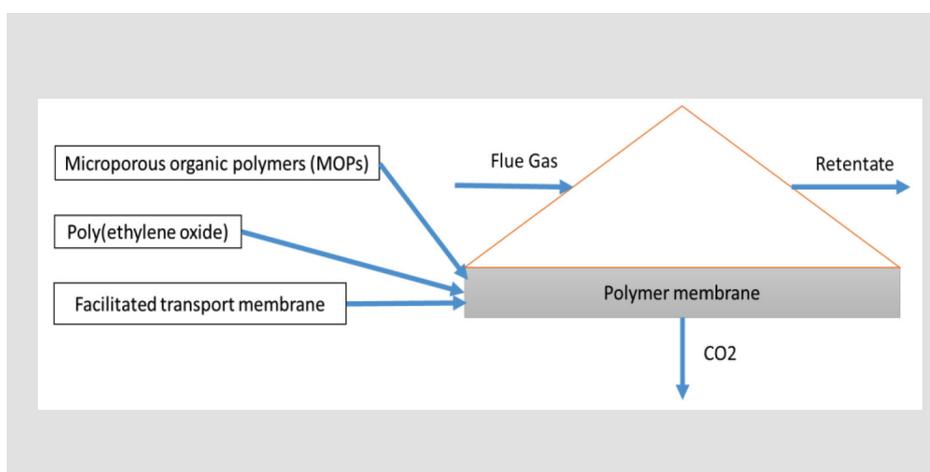
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1. Introduction

The United Nations Framework Convention on Climate Change (UNFCCC) calls for the stabilization of greenhouse gas (GHG) concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system. The Kyoto Protocol to the Convention commits its parties to binding targets based on a 'basket' of six GHGs, including carbon-dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF₆) [1]. Carbon dioxide has become a major environmental

concern due to the gradual increase of its global atmospheric concentration in recent decades. With the rapid increase of the global population and the industrialization of more and more countries, the consumption of energy is explosively growing. Currently over 85% of the global energy demand is being supported by the burning of fossil fuels [2]. Fossil fuels will continue to play an important role in the foreseeable future, mainly in power generation and industrial manufacturing. The estimation from the Intergovernmental Panel on Climate Change (IPCC) has shown that CO₂ emissions could be reduced by 80–90% for a modern power plant that is equipped with suitable

GRAPHICAL ABSTRACT



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carbon dioxide capture and storage (CCS) technologies [3]. Depending on the generation of CO₂, several capture options and tendentious technologies have been suggested and implemented. Generally, based on the fundamental chemical process involved in the combustion of fossil fuels, three basic CO₂ separation and capture options were adopted: (1) pre-combustion capture; (2) oxy-fuel combustion; and (3) post-combustion capture [2]. Post-combustion capture requires removing CO₂ from flue gas, comprised mainly of N₂ and CO₂, before emission into the atmosphere. Post-combustion capture is the most feasible on a short time scale because many of the proposed technologies can be retrofitted to existing fossil fuel consuming power plants. Absorption, cryogenic distillation, biological methods and adsorption and membrane-based separation are the currently used technologies and methods in CO₂ separation [4]. Absorption (i.e. solvent scrubbing) is a well-established CO₂ separation approach used in the chemical and petroleum industries today [5]. Cryogenic distillation uses a principle of separation based on cooling and condensation, and has been used in liquid separations for a long time. This technique is theoretically sound for CO₂ separation; however, the considerable energy demand deems it unreasonable for practical application. Algal bio-fixation of CO₂ in photo-bioreactors has, for example, recently gained great interest in CO₂ capture. It is evident that the progress and achievement of almost all of these technologies relies heavily on the development of materials. The challenges that arise in the development of these materials and techniques lie in being able to transfer the technology from the lab to the harsh conditions of the industry that will be subjected to while maximizing efficiency and minimizing costs [4]. Conventional solid adsorbents include activated carbons, silica gel, ion-exchange resins, zeolites, and meso-porous silicates, activated alumina, metal oxides, carbon fibers, metal-organic frameworks and other surface-modified porous media. A recent review has comprehensively described the adsorbent materials for CO₂ capture from large anthropogenic point sources [6]. Rapid Temperature Swing Adsorption (RTSA) processes offer potential techniques for the capture of CO₂ from flue gas mixtures [7-12]. Apart from the physical and chemical methods mentioned above, biological methods have also been proposed for CO₂ separation [13, 14]. Membrane-based separation is based on the differences in physical and/or chemical interactions between gases and the membrane material, which can be modified to allow some components to pass

preferentially through the membrane based on size (kinetic) and/or affinity (thermodynamics). In general terms, the membrane materials for pre- and post-combustion CO₂ capture (see Figure 1) can be classified into three main families: (1) polymers, (2) dense or metal membranes, and (3) porous inorganic membranes [15]. This classification should not be regarded as absolute, since examples of hybrid membranes including combinations of these three families are frequent and even desired for merging the general advantages of each individual family. This is the case, for instance, of mixed matrix membranes (MMMs) consisting of a polymer matrix doped with solid particles, or hybrid silicas consisting of a silica matrix, usually micro- or meso structured, impregnated or doped with a polymer. Membranes have a great potential in CO₂/H₂ separation in pre-combustion capture and post-combustion CO₂/N₂ separation. A wide variety of different membrane materials and processes are available, some of which are already on an industrial scale, and potentially applicable in CO₂ separation. The performance and associated cost of these membrane-based technologies in large scale CO₂ capture mainly relies on the membrane materials themselves [4]. Inorganic ceramic membranes and organic polymeric membranes have been used in CO₂ separation from flue gas in post-combustion. However, reaching a high degree of CO₂ separation by using a single-stage ceramic or polymeric membrane is difficult as of yet (although it is feasible in terms of cost). New materials are still required to achieve the desired effectiveness in CO₂ separation by membranes. Gas separation based on adsorption has been well developed, in which the selection of a sound adsorbent is the key for specific separation.

The three basic technologies for CO₂ separation: absorption, adsorption, and membrane processes have been extensively studied, using the amine-based absorption process as the current bench mark. Despite the intensive investigation, however, no single technology has been demonstrated to be capable of meeting the requirements set by the DOE/NETL: 90% CO₂ capture at less than a 35% increase in the cost of electricity [16, 17]. Membrane-based CO₂ separation is one of the most energy efficient ways to capture CO₂ [18]. However, the traditional polymer membranes suffer from low CO₂/N₂ selectivity (less than 100). Currently, CO₂ capture by gas-separation membranes is not as effective as other CO₂ recovery methods because of the low permeability and selectivity of commercially available membranes [19].

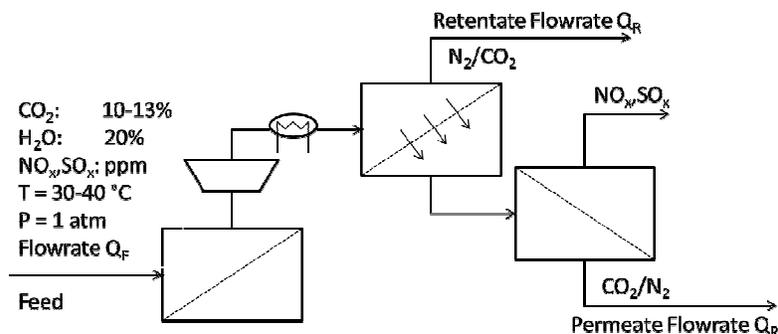


Fig. 1. Post combustion CO₂ capture using membrane separation with feed pressurization [15].

The polymer materials are based on polymer membranes and related materials. Polymer membranes and hollow fibers (e.g., cellulose, polyarylate, polypyrrolone, polyimide, polysulfone, polycarbonate, poly-(ethylene oxide), and poly(ether imide)) have been widely investigated for gas separation applications [15, 20-25]. The application of polymer membranes to CO₂ separation is usually argued as limited due to their insufficient thermal, mechanical, and chemical stabilities and their intrinsic low permeances. Separation of gas pairs in polymeric membranes is defined by the selectivity, α_{ij} , which is the ratio of the permeability of the faster gas (P_i) to the slower gas (P_j). Selectivity can be decoupled into solubility-selectivity and diffusivity-selectivity, $\alpha_{ij} = P_i/P_j = (S_i/S_j) \times (D_i/D_j)$. An improvement in selectivity can be achieved by a combination of greater gas diffusivity selectivity or increasing the solubility of the faster gas in the polymer. Previous work has attempted to increase the selectivity mainly by improving diffusivity-selectivity through an increase in the chain rigidity or by tuning cavity size [26, 27]. On the other hand, increasing the solubility selectivity of the "faster gas" has also attracted great interest [28, 29]. As such, even modest increases in solubility-selectivity can lead to significant improvements in overall selectivity. For the specific application of CO₂ capture from the flue gas, it has been reported that a CO₂/N₂ selectivity of >70 and a minimum CO₂ permeability of 100 Barrers (1 Barrer = 10⁻¹⁰ cm³(STP) cm (cm² s cmHg)⁻¹) for a membrane thickness of 0.1 μm (a permeance of 1000 GPU (gas permeation unit), where 1 GPU = 10⁻⁶ cm³(STP)/(cm² s cmHg)) are required for the

economic operation [30, 31]. As an alternative to conventional polymeric membranes, facilitated transport membranes have shown better promise to satisfy these goals [32-34]. A comprehensive survey of glassy and rubbery membrane implementation in pre- and post-combustion processes can be found in some excellent reports [20-25].

As mentioned above it is highly desirable to develop advanced membranes with high CO₂/N₂ selectivity. Cost effectiveness may be achievable only when separation is promoted by a CO₂ selective chemical reaction. A number of polymer types have shown good gas transport properties and considerable scope for structural variations. In this section, only the polymers with CO₂/N₂ selectivity >30 and CO₂ permeability > 40 Barrer are summarized. Other works related to the polymeric membrane for CO₂ capture such as polymer membranes surface modification for CO₂ capture [35], mixed matrix membranes [36] and membrane absorption [37, 38] will not be discussed here.

2. Microporous organic polymers (MOPs)

Microporous organic polymers (MOPs) are of potential technological significance for gas storage, gas separation and low-dielectric applications [26, 39-43]. MOPs can be classified either as amorphous polymers (for example, substituted polyacetylenes [38]), thermally rearranged polymers [26,

27], and polymers of intrinsic microporosity (PIMs) [35, 39] or as crystalline polymers [47, 48]. For membrane-based gas separation, solution-processable, amorphous MOPs are required for practical membrane fabrication such as thin-film composites. Among MOPs, poly(1-trimethylsilyl-1-propyne) (PTMSP) is known as the highest gas-permeable polymer. However, PTMSP shows low gas selectivity [39] and also suffers from fast physical ageing, leading to a catastrophic reduction in gas permeability, because the initially formed microporous structures are rapidly corrupted by equilibrium processes.

Guiver and his co-worker [43] selected PIM-1 as a MOP platform for post-polymerization modification owing to its simple structure, ease of preparation, high molecular weight and good mechanical strength. PIM-1 contains two nitrile groups per repeat unit, which is the reaction site for functionalization as shown in Figure 2 [43]. They show a class of amorphous MOP, prepared by [2 + 3] cycloaddition modification of a polymer containing an aromatic nitrile group with an azide compound, showing super-permeable characteristics and outstanding CO₂ separation performance, even under

polymer plasticization conditions such as CO₂/light gas mixtures. The unprecedented result arises from the introduction of tetrazole groups into highly microporous polymeric frameworks, leading to more favorable CO₂ sorption with superior affinity in gas mixtures, and selective CO₂ transport by presorbed CO₂ molecules that limit access by other light gas molecules. This strategy provided a direction in the design of MOP membrane materials for economic CO₂ capture processes [43].

Guiver et al. demonstrated MOPs functionalized with CO₂-philic pendant tetrazole groups (hereafter referred to as TZPIMs) [43]. The TZPIM membranes demonstrate exceptional gas separation performance, surpassing the most recent upper bounds [49] of conventional and state-of-the-art polymeric membranes for the important gas pairs, such as for example the CO₂/N₂ separation. TZPIM1 and TZPIM2 have CO₂/N₂ selectivities around 31 and 33 and CO₂ permeabilities around 2250 and 3000 Barrer, respectively [43].

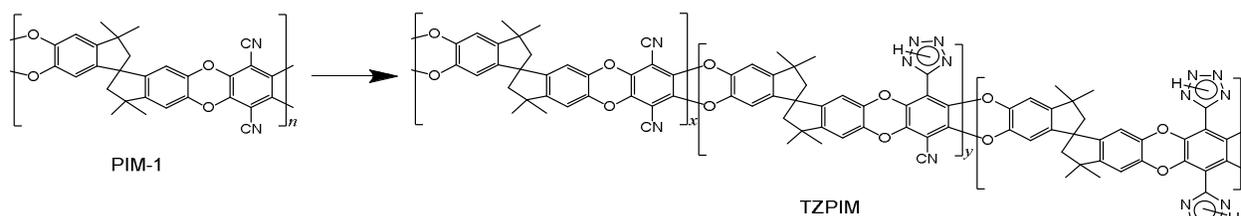


Fig. 2. Conversion of PIM-1 to TZPIM via the [2+3] cycloaddition reaction between aromatic nitrile groups and sodium azide, producing a tetrazole functional group [43].

According to a recent estimate [50], at CO₂/N₂ selectivities above 40, a 4,000 GPU membrane could offer a capture cost below \$15/ton CO₂, which is lower than the US Department of Energy's (DOE) target goal of \$20/ton CO₂ [51]. Based on the CO₂ permeability of a dense, thick TZPIM film (2,000 Barrers), if TZPIM thin-films below 0.5 μm can be successfully fabricated in the form of thin film composite membranes, and the separation performance can be verified in real flue gas compositions that include water, TZPIM membranes will provide a viable energy-saving alternative for CO₂ capture from flue or fuel gas that is within current DOE cost targets. However, a substantial hurdle exists before polymeric membranes can be used for practical CO₂ separations, such as selective CO₂ removal from flue gas, biogas refining, and natural gas sweetening. In gas mixtures, the gas selectivity is typically much lower than permselectivity from single gas permeation data because of CO₂ plasticization and/or competitive sorption effects [26]. That is, CO₂ molecules cause the polymer matrix to swell, leading to increased permeability of the slower gas beyond its pure gas permeability and resulting in reduced selectivity [43]. In addition to numerous advantages, MOPs present a range of challenges. Some MOPs are relatively expensive. An associated problem is environmental impact, since most organic polymer chemistry is carried out using volatile organic solvents. For a long-term "life cycle" perspective, the environmental degradability of the aromatic units that comprise most MOPs is poor [44].

3. Poly(ethylene oxide) and its cross-linked polymer, copolymers and polymer blend dense films membranes

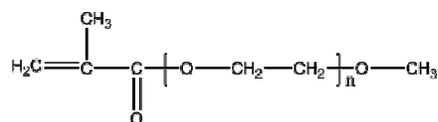
Yoshino et al. have examined a number of high molecular weight branched poly(ethylene oxide)-based polymers [72]. These polymers were synthesized by using a combination of various monomers; ethylene oxide (EO), 2-(2-methoxyethoxy)ethyl glycidyl ether (EM) and Allylglycidyl ether (AGE).

Table 1
Carbon dioxide and nitrogen gas permeability data for poly(ethylene oxide) dense films at 35 °C [52].

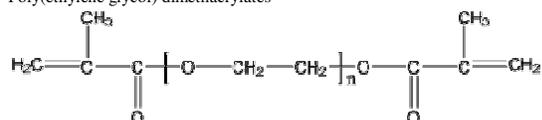
Name	P(CO ₂) (barrer)	P(N ₂) (barrer)	α(CO ₂ /N ₂)
EO/EM/AGE (80/20/2)	773	16.8	46
EO/EM/AGE (77/23/2.3)	680	15.5	44
EO/EM/AGE (96/4/2.5)	580	12.1	48

Table 2
Monomers used by Hirayama et al. [53].

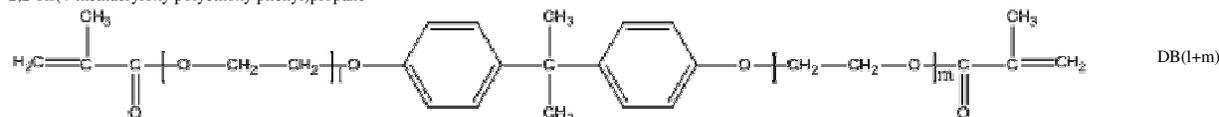
Poly(ethylene glycol) methyl ether methacrylate



Poly(ethylene glycol) dimethacrylates



2,2-bis(4-methacryloxy polyethoxy phenyl)propane



These polymers give very good combinations of carbon dioxide permeabilities and selectivities, with one example possessing a carbon dioxide permeability of 773 Barrer and a CO₂/N₂ selectivity of 46 as shown in Table 1. Since the gas transport properties of these materials were tested at different pressures and temperatures for the majority of the gas permeability literature, a direct comparison of gas transport properties is difficult [20]. Cross-linking offers the potential to improve the mechanical and thermal properties of a membrane. Koros and Mahajan have suggested that cross-linking can be used to increase membrane stability in the presence of aggressive feed gases and to simultaneously reduce plasticization of the membrane [24].

Hirayama et al. have investigated the effects of cross-linking poly(ethylene oxide) on the carbon dioxide and nitrogen gas transport properties [53]. Methacrylate terminated monomers incorporating poly(ethylene oxide) of various lengths (Table 2) were photo polymerized. All of the polymers gave good CO₂/N₂ selectivities, and most exhibited large CO₂ permeabilities at temperatures up to 100 °C. Table 3 listed cross-linked poly(ethylene oxide) gas permeability data.

Table 3
CO₂ and N₂ gas permeability data for cross-linked membranes dense films at 25 °C, feed pressure of 96.7 kPa [53].

Name	P(CO ₂) (barrer)	P(N ₂) (barrer)	α(CO ₂ /N ₂)
DM14/MM9 (100/0)	45	0.66	68
DM14/MM9 (90/10)	62	0.90	69
DM14/MM9 (70/30)	96	1.5	66
DM14/MM9 (50/50)	144	2.25	64
DM14/MM9 (30/70)	210	3.3	63
DB30/MM9 (100/0)	93	1.5	63
DB30/MM9 (90/10)	105	1.6	64
DB30/MM9 (70/30)	141	2.1	67
DB30/MM9 (50/50)	179	2.9	62
DB30/MM9 (30/70)	250	4.2	60
DM23/MM9 (90/10)	145	2.2	66
DB69/MM9 (90/10)	240	4.3	56
DM14/MM23 (30/70)	240	3.9	62

Copolymers offer the potential to fine tune permeabilities and reduce the costs of polymer synthesis. A copolymer will tend to have permeabilities which are intermediate compared with the homopolymers which make it up. Likewise, an expensive and effective polymer can have a significantly reduced price by the formation of a copolymer which incorporates cheaper monomers. The CO₂/N₂ gas separation properties of a large series of poly(ethylene oxide) segmented copolymers with polyurethanes, polyamides and polyimides have been investigated by Okamoto and co-workers [54] and listed in Table 4. These copolymers generally gave both high selectivities and a high CO₂ permeability, likely due to the high solubility of carbon dioxide into the poly(ethylene oxide) segments. Of particular note is the polymer PMDA-pDDS/PEO4(80) (Figure 3) which exhibits a CO₂ permeability of 238 Barrer and a CO₂/N₂ selectivity of 49. This combination of both high selectivities and permeabilities may be related to the low pressures used during the determination of the gas transport properties.

Permeabilities of polymers are most often reported at a temperature of 35

°C. Upon decreasing the measuring temperature, the gas permeation values have been observed to drop. This drop in gas permeation values was very strong for the PEO polymer if the PEO segments started to crystallize. A practical lower limit temperature for use of the block copolymers in gas separation is the PEO melting temperature, and this rules out the use of long PEO segments, which have high melting temperatures [55].

4. Facilitated transport membrane

Current CO₂-selective membranes are based on either the solution-diffusion mechanism or facilitated transport mechanism. In recent years, facilitated transport membranes are of interest because of their potential to achieve high selectivity without sacrificing permeability. This type of membrane is based on the reversible reactions between reactive carriers and CO₂ in the membranes. The facilitated transport membrane has been successfully patented for its promising application in CO₂ capture [56-58]. Based on this process, the membrane has a support coated and cross linked polyvinylamine, which serves as a fixed carrier of CO₂ and a "catalyst", that helps to quickly remove and transport CO₂ through the membrane lumen. It is reported through the improvement of this process that CO₂/N₂ selectivity has approached 174 and 200 by the same research group [59, 60].

Ho and coworkers [61] have also come up with the similar approaches of cross linking. A novel CO₂-selective membrane with the facilitated transport mechanism has been synthesized to capture CO₂ from the industrial gas mixtures, including flue gas. Both mobile and fixed amine carriers were incorporated into the cross-linked poly(vinyl alcohol) (PVA) during the membrane synthesis. Examples of the chemical structure of carriers and the related reactions are as shown in Table 5 and Equations (1)-(3) [61].

Table 4
CO₂ and N₂ gas permeability data for copolymers and polymer blend dense films at 35 °C and 2 atm [54].

Name	P(CO ₂) (barrer)	P(N ₂) (barrer)	α(CO ₂ /N ₂)
MDI-BPA/PEG(80)	48	1.0	47
MDI-BPA/PEG(85)	59	1.20	49
LTDI(20)-BPA/PEG(90)	47	0.92	51
LTDI(40)-BPA/PEG(85)	35	0.73	48
IPA-ODA/PEO3(80)	58	1.1	53
BPDA-ODA/DABA/PEO2(80)	36	0.64	56
BPDA-ODA/PEO3(75)	75	1.4	52
BPDA-mDDS/PEO3(75)	72	1.4	53
BPDA-mPD/PEO4(80)	81	1.5	54
BPDA-ODA/PEO4(80)	117	2.3	51
PMDA-ODA/PEO2(75)	40	0.74	54
PMDA-mPD/PEO3(80)	99	2.0	50
PMDA-APPS/PEO3(80)	159	3.1	51
PMDA-APPS/PEO4(70)	136	2.6	53
PMDA-mPD/PEO4(80)	151	2.9	52
PMDA-ODA/PEO4(80)	167	3.2	52
PMDA-pDDS/PEO4(80)	238	4.9	49

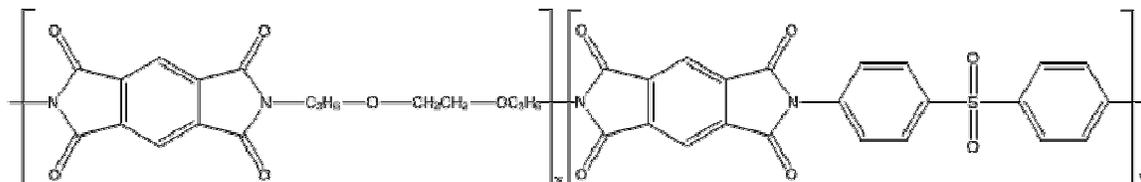
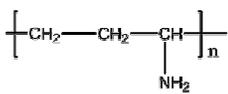
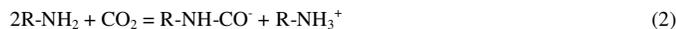
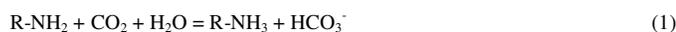


Fig. 3. PMDA-pDDS/PEO4(80) [54].

Table 5
The chemical structure of carriers [61].

Mobile carriers:	Potassium carbonate-Potassium bicarbonate: K_2CO_3 - $KHCO_3$ 2-Aminoisobutyric acid-potassium salt: $NH_2C(CH_3)_2COO^-K^+$
Fixed carrier:	Poly(allylamine): 



Amines in cross linked poly (vinyl alcohol) of the polymeric membrane reached CO_2/N_2 selectivity of 450 and the membrane has a descent performance even at the temperature range of $100\text{ }^\circ\text{C} - 170\text{ }^\circ\text{C}$, much higher than the current prevalent working temperature of the polymer membrane [51]. Highly hydrophilic compounds containing quaternary ammonium moieties attached to the reactive trimethoxysilane have CO_2/N_2 selectivity up to 1500 and the permeability increased by 35 fold in moisture than that of the dry mode without CO_2/N_2 loss [62]. If these encouraging results are sustainable for extended periods of operation, such systems will merit serious consideration as candidates for CO_2 capture at coal-fired power plants. Modeling results indicate that facilitated transport membranes could capture CO_2 efficiently even in the concentration of as low as 10% in flue gas, with 90% efficiency, 90% CO_2 purity with competitive cost to that of aqueous amine scrubbing [61].

In 2008, Ho and coworkers [63] synthesized a novel CO_2 -selective membrane with the facilitated transport mechanism to capture CO_2 from the industrial gas mixtures, including flue gas. Both mobile and fixed amine carriers were incorporated into the cross-linked poly(vinyl alcohol) (PVA) during the membrane synthesis. The crosslinking of PVA with formaldehyde is a condensation reaction, which is shown schematically in Figure 4 [63]. Free polyallylamine was prepared by mixing poly(allylamine hydrochloride) with a stoichiometric amount of KOH in methanol overnight. 2-Aminoisobutyric acid (AIBA) potassium salt (AIBA-K) was synthesized by mixing AIBA with a stoichiometric amount of KOH in DI water for 30 min. The chemical structures of these compounds are illustrated in Figure 5 [63].

The membrane showed desirable CO_2 permeability (with a suitable effective thickness) and CO_2/N_2 selectivity up to $170\text{ }^\circ\text{C}$. In the CO_2 capture experiments from a gas mixture with N_2 and H_2 , a permeate CO_2 dry concentration of $>98\%$ was obtained, using steam as the sweep gas. A one-dimensional isothermal model was established to examine the performance of

a hollow-fiber membrane module composed of the described CO_2 selective membrane. The modeling results show that a CO_2 recovery of $>95\%$ and a permeate CO_2 dry concentration of $>98\%$ are achievable from a 1000 standard cubic feet per minute (SCFM) (or 21.06 mol/s) flue gas stream with a 2 ft (0.61 m) hollow-fiber module that contained 980 000 fibers [63].

In 2013, new CO_2 -selective facilitated transport membranes were synthesized by incorporating poly-N-isopropylallylamine, a moderately hindered polyamine as the CO_2 fixed-site carrier, and CO_2 mobile carriers into the cross-linked PVA-poly(siloxane) membrane matrix by the same research group [64]. CO_2 -selective facilitated transport membranes with a thin-film-composite structure were synthesized by the solution casting technique [61, 65]. In a particular experiment, 3.4 g of as-received polyvinylalcohol (PVA) was dissolved in 18 g of deionized water at room temperature under minor stirring overnight. One gram of (3-aminopropyl) triethoxysilane (APTEOS) and 0.15 g of hydrochloric acid (HCl) were added to the aqueous PVA solution and the acid-catalyzed sol-gel reaction was carried out at $80\text{ }^\circ\text{C}$ for 80 min under vigorous stirring to produce the PVA-poly(siloxane) hybrid matrix [66]. The sol-gel reaction and the cross-linking reaction are described in Figure 6. The new membrane exhibited significantly enhanced performance and long-term stability in CO_2/H_2 and CO_2/N_2 separations under relatively high temperatures. At $110\text{ }^\circ\text{C}$ and a feed pressure of 2 atm, it showed a high CO_2 permeability of greater than 6500 Barrers, CO_2/H_2 selectivity of more than 300 and CO_2/N_2 selectivity of at least 650. Better membrane separation results were achieved as sweep-side water content was increased. The membrane also showed good stability of at least 430 h at $110\text{ }^\circ\text{C}$ and 2 atm. The membrane performance reduced as temperature was increased from 107 to $180\text{ }^\circ\text{C}$ due to the reduction of the water retention ability of the membrane; however, it still held a good CO_2/H_2 selectivity of about 34 at $180\text{ }^\circ\text{C}$ [64].

The limitation of facilitated transport membranes are Carrier stability, feed preconditioning and carrier saturation phenomenon [67].

The market for CO_2 separation is currently dominated by polymeric membranes due to their relatively low manufacturing cost and processing ability into flat sheet and hollow fiber configurations as well as well-documented research studies. Most membrane materials do not have the resilience to industry conditions and quickly fail. Research into producing durable resilient materials is the main focus for industrial applications. The new generation of membranes must be able to maintain its durability in rigorous environments, e.g. good mechanical stability at high feed pressure/temperature and high resistance to plasticization, to ensure a long-term stable operation. Moreover, a highly permeable membrane with high selectivity for CO_2/CH_4 is developed [67]. The goal is to develop facilitated transport membranes that can maintain its permeability and selectivity without the preconditioning of moisture in the feed stream. CO_2 carrier stability in terms of degradation and evaporation should be improved, especially for mobile carrier membranes. The dependence of CO_2 partial pressure on CO_2 permeance should also be minimized [67].

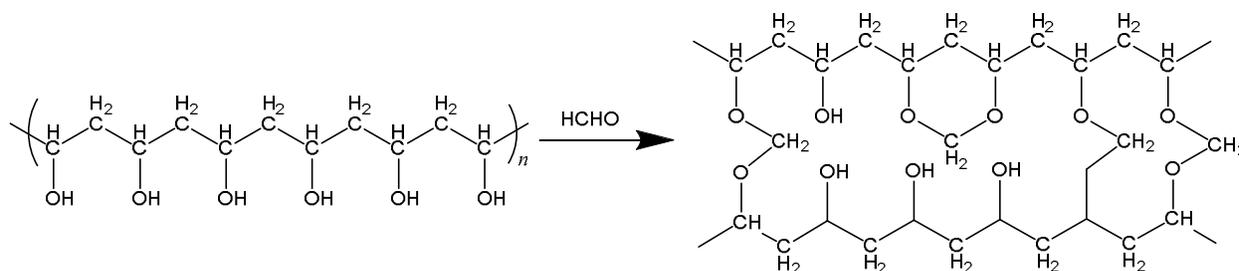


Fig. 4. Synthesis of the cross-linked PVA with formaldehyde [63].

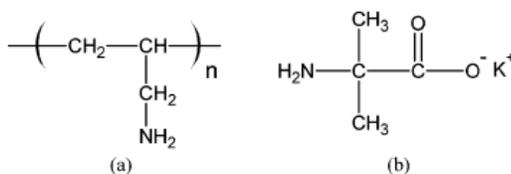


Fig. 5. Chemical structures of (a) free polyallylamine and (b) AIBA-K [63].

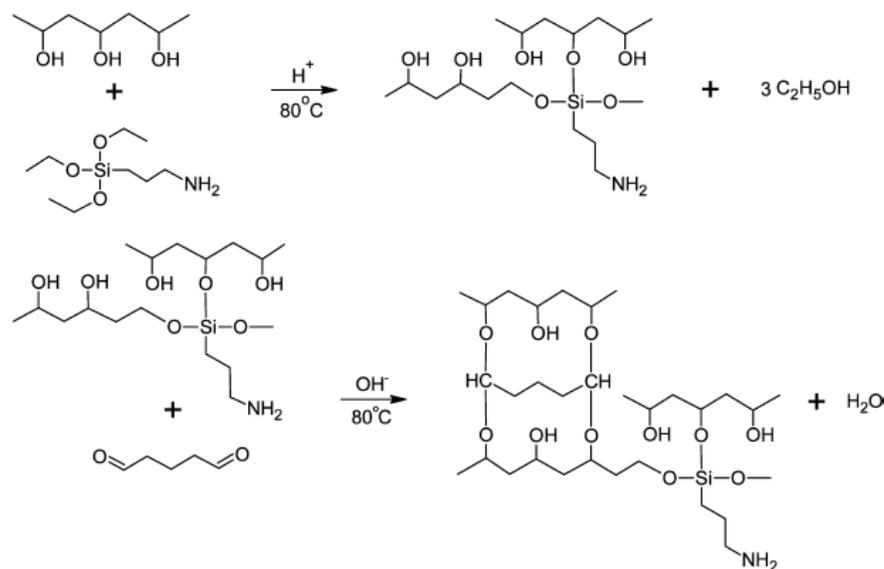


Fig. 6. Sol-Gel Reaction and Crosslinking Reaction for PVA [66].

6. Conclusions

CO₂ capture is attracting the broad attention of both science and technology. This review concentrates on flue gas CO₂/N₂ separation, so the CO₂ capture related gas separation polymeric membranes with high CO₂ permeabilities and CO₂/N₂ selectivities have been discussed. Three kinds of polymer membranes were discussed. They are microporous organic polymers (MOPs), Poly(ethylene oxide) and its cross-linked polymer, copolymers and polymer blend dense films membranes and the facilitated transport membrane. Based on the above polymers, more modification or a combination with other materials such as the mixed matrix membrane can be developed to discover new membrane materials for CO₂ capture. Additionally, while gas transport properties are important, it is equally important to ensure that membranes are physically durable and resistant to both chemical attack and plasticization, while still being flexible enough for manufacture into various membrane types. For this reason, it is expected that future research will concentrate on improving these properties through techniques such as crosslinking after manufacture into appropriate membrane morphology.

7. References

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