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Review

# Recent progress of fillers in mixed matrix membranes for $CO_2$ separation: A review

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ABSTRACT

Among various $CO_2$-mitigation technologies, membrane-based technology has offered a more energy efficient and eco-friendly process for $CO_2$ separation from large emission sources, in order to reduce $CO_2$ emission level into atmosphere. In general, polymeric and inorganic membranes have been used in gas separation processes, but each has its own pros and cons. Currently, membrane research has addressed the trade-off limitations of membranes in different ways through fabrication of new type of mixed matrix membranes (MMMs) by incorporation of inorganic particles as fillers into polymer matrices. The performance of MMMs depends on textural properties of fillers, molecular sieving effect and membrane–penetrant interactions. The main challenges in the fabrication of MMMs is selection of fillers, which controls the gas separation characteristics of membranes. In this review, the influences of fillers like zeolite, carbon, and metal organic framework in MMMs fabrication and their $CO_2$ permeability and $CO_2/CH_4$ and $CO_2/N_2$ selectivity were compiled from recent reports. Further, a new protocol is introduced for screening of fillers, which will helps to development of new fillers as well as for fabrication of new MMMs with high $CO_2$ separation capacity.

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*Abbreviations:* CA, cellulose acetate; β-CD, beta-cyclodextrins; CCS, carbon capture and sequestration; COK, Centrum voor Oppervlaktechemie en Katalyse; CMS, carbon molecular sieves; CNFs, carbon nanofibers; CNTs, carbon nanotubes; ETS, engelhardt titanosilicate; 6FDA-DAM, 2,2-bis(3,4-carboxyphenyl) hexafluoropropane dianhydride-diaminomesitylene; GO, graphene oxide; GPU, gas permeation unit; GTA, glycerol triacetate; IL, ionic liquids; IPCC, Intergovernmental Panel on Climate Change; MCM, mobil composition of matter; MFI, mordenite framework inverted; MWCNTs, multi-walled carbon nanotubes; MIL, materials institute lavoisier; MMMs, mixed matrix membranes; MOFs, metal organic frameworks; PDMS, polydimethylsiloxane; PEBA or PEBAX, poly(ether-block-amide); PEI, polyethylenimine; PEG, poly(ethylene glycol); PEO, poly ethylene oxide; PES, polyethersulfone; PF, permeability factor; PI, polyimide; PIM, polymers of intrinsic microporosity; PMP, poly(4-methyl-1-pentyne); PMPS, polymethylphenylsiloxane; POZ, poly(2-ethyl-2-oxazoline); PSf, polysulfone; PVC-g-POEM, poly(vinyl chloride)-g-poly(oxyethylene methacrylate); PVDF, poly(vinylidene fluoride); PU, polyurethane; SAPO, sodium-alumino-phosphate; SF, separation factor; SBA, santa barbara amorphous; SWCNTs, single walled carbon nanotubes; SEBS, polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene; SPEEK, sulfonated poly(ether ether ketone); TS, titanium silicalite; UiO, University of Oslo; UNFCCC, United Nations Framework Convention on Climate Change; ZIF, zeolitic imidazolate framework; ZSM, zeolite socony mobil.

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## 1. Introduction

The current world energy demand and industrialization requires a large amount of fossil fuel, which results in enormous $CO_2$ emission into the atmosphere from power plants, ends up in major changes in the biological world, and affects all levels due to trapping the earth's surface temperature resulting in global warming. Intergovernmental Panel on Climate Change (IPCC) report has projected that by the year 2035, $CO_2$ level will increase to 450 ppm, which will lead to a chance of increase in 2 °C global temperature [1]. It also reveals that the global increase rate of $CO_2$ is about 11.7 ppm from 2005 to 2011, and based on the predictions of the simulation model, globally averaged $CO_2$ from the preindustrial era to the present increases by 794–1149 ppm by the year 2100 [2]. According to the Keeling curve, each 188 million tons of $CO_2$ emission contributes to raise in 1 ppm of atmospheric $CO_2$ concentration and the level reached 408.84 ppm in June 2017 [3]. The United Nations Framework Convention on Climate Change (UNFCCC) COP 21 (Conference of Parties) at Paris, December 2015, has set a task for all countries to control the increasing atmospheric warming well below 2 °C and move to a low carbon pathway for energy production [4]. The major $CO_2$ emitters are energy sectors, steel and cement industries, and the existing mitigation policies in these sectors are mainly focused on increasing energy efficiency processes, switching to low carbon-intensive sources of energy, and carbon capture and sequestration (CCS). Further, the refineries have also been marked as huge $CO_2$ emitting sectors due to the unregulated pumping of $CO_2$ in refineries. Compared to other sources, about 4% of the global $CO_2$ emissions, close to 1 bmt $CO_2$/year, has been contributed by the refineries, which ranked 3rd among stationary $CO_2$ producers [5]. Thus, there is an urgent need to develop $CO_2$ mitigation processes, and it becomes mandatory at all levels of $CO_2$ emission sources. A number of technologies have been employed for $CO_2$ removal, such as pre-combustion, post-combustion, and oxy-fuel combustion. Among these, the post-combustion $CO_2$ capture is generally compatible with CCS activity which includes, commercial absorption technique by alkanolamines [6–8], adsorption [9–11], chemisorption [12,13], membrane separation [14,15], cryogenics separation [16,17], and enzymatic [18–20] processes; still they have their own demerits like corrosive nature, low $CO_2$ separation yield, high cost regeneration process, etc.

In fact, the interest for commercial $CO_2$ separation and capture can be efficiently achieved by membrane technology, which has been evolved as a competitive technique in energy production and natural gas industries [21–23]. It is fairly reported that membrane process has inherent attributes like low energy consumption with continuous operation, cost-effectiveness, and process flexibility compared to the traditional methods [24,25]. Membrane performances can be categorized based on various aspects such as separation mechanism, nature and structure of materials. Further, diffusion phenomena are also governed by the morphological and physical properties such as total pore volume, pore size distribution, average pore diameter, and pore length of membrane. These textural properties are innate characteristics, which depend on the type of membrane materials, and can be subjected to surface enrichment or modifications. In general, molecular diffusion depends on the diameter and the length of molecules [26,27]. Fig. 1 shows the kinetic diameter of various gas molecules and pore diameter required for their separation.

Many new membranes are still being developed for rapid $CO_2$ separation from emission streams. Generally, polymeric membranes are used for $CO_2$ separation due to cost-effective process, durable in industrial processing, energy efficient, and flexible compared to the other available $CO_2$ separation processes. Upon fabrication with either glassy or rubbery materials, polymer membranes can achieve better $CO_2$ separation based on molecular sieving by difference in size and diffusion principle [28,29]. Further, rubbery material separates components based on condensability whereas the glassy material stringently separate gases based on difference in size or kinetic diameter [28,30]. Thus, the glassy polymers perform better in gas selectivity with high permeability than rubbery polymers. However, the polymeric membranes have restrictions due to their "trade-off" between permeability and selectivity of gases, these limitations have been resolved and the productivity of polymeric membrane might be improved by the modification of polymeric membranes, which could diminish the selectivity or vice versa [31,32].

Inorganic membranes possess molecular sieve-like properties show significantly higher diffusivity and selectivity of gas molecules compared to polymeric membranes due to their discriminating ability based on pore size and shape. Further, these inorganic membranes are advantageous in terms of thermal and chemical stability, mechanical strength, and longer lifespan [33]. Specifically, inorganic membranes efficiently favor $CO_2$ separation because of their narrow pore size distribution, and high operating temperature and pressure. Yet, the other parameters of these membranes, such as fabrication of defect-free membrane for