

Amine Type in CO₂ Separation

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Efficient CO₂ capture technologies such as absorption/adsorption of CO₂ sorbents, cryogenic separation, and membrane separation, have been developed experimentally and industrially. Among them, membrane technology is attracting growing attention owing to its inherent advantages that include energy-efficiency, ease of operation and scale-up, and a small footprint.

Keywords: carbon dioxide separation ; organosilica membrane ; amine type ; sterical hindrance ; activation energy for permeation

1. Introduction

The ever-increasing rate of greenhouse gas emissions in the atmosphere, particularly CO₂ generated from the combustion of fossil fuels, has led to serious global climate concerns. Therefore, efficient CO₂ capture technologies such as absorption/adsorption of CO₂ sorbents, cryogenic separation, and membrane separation, have been developed experimentally and industrially over the past few decades. Among them, membrane technology is attracting growing attention owing to its inherent advantages that include energy-efficiency, ease of operation and scale-up, and a small footprint [1][2][3][4][5]. As one of the most important members of the membrane family, organosilica membranes have been applied to various membrane processes with superior separation performance and a high tolerance to harsh conditions. Typical organosilica membranes developed for CO₂/N₂ separation are either microporous with rigid pores or nonporous with “free-volume” pores. Separations are therefore achieved mainly by the effect of molecular sieving along with partial contributions from selective surface diffusion through rigid pores and/or solution-diffusion within a nonporous structure. The selectivity is always less arresting due to the comparable kinetic diameters of CO₂ (3.3 Å) and N₂ (3.64 Å) and due as well to the difficulty in precisely controlling the pore (rigid or free-volume type) sizes. Given this, various amine-functionalized silica-based membranes have been developed to accomplish CO₂ separation from gas mixtures with potentially enhanced efficiency [6][7][8][9][10][11][12][13]. These membranes are expected to show great potential in simultaneously promoting CO₂ permeance and permselectivity due to the reversible reactions between CO₂ and amine groups. Thus far, however, only a limited number of membranes have offered appealing CO₂ separation performance with both high CO₂ permeance and CO₂/gas permselectivity irrespective of many reports of amine-functionalized silica-based membranes. Instead, in some cases even reverse CO₂/N₂ selectivity under a dry state has been observed [13]. Whereas, in some cases, other types of membranes with only CO₂-philic groups rather than chemical reactions, such as poly(ethylene oxide)-based membranes, have resulted in attractive CO₂ separation performance [2]. Hence, further fundamental studies in terms of the effect of amine-CO₂ chemical interactions on CO₂ transport behaviors through amine-functionalized silica-based membranes are needed to direct the fabrication of high-performance CO₂ separation membranes.

In general, how fast and selectively the species to be separated can enter into, transport through, and exit from the membrane govern the membrane separation properties in terms of both flux and selectivity. Therefore, the reaction activities of amine groups (or membrane affinity) should be regarded in a broad sense, comprising not only the favorable and rapid reaction/interaction with CO₂ molecules but also the promoted/inhibited motion of CO₂ within amine-containing membranes. Consequently, to push the CO₂ separation performance (or transport efficiency) of these membranes to the limit, the first idea to keep in mind in the design process should be to choose an amine-containing material with a convenient affinity for CO₂ molecules. In fact, the effects that amine type (primary, secondary, and tertiary), basicity (or *pK_a*), and steric hindrance can exert on CO₂ sorption performance in terms of absorption/adsorption capacity and rate, as well as energy cost during the CO₂ regeneration/release process, have been extensively studied in the field of amine-based CO₂ sorbents (solid adsorbents or aqueous alkylamine solutions) [14][15][16][17]. It is common knowledge that tertiary and/or sterically hindered amines in some cases could exceed the trade-off between the heat of reaction and the CO₂ absorption rate (see **Figure 1**), which thus enables energy-saving CO₂ sorption and release processes. Theoretically, this phenomenon could offer innovations for the design and development of amine-containing CO₂ separation membranes

that integrate CO₂ adsorption, diffusion, and desorption processes into a thin membrane layer. Indeed, Prof. Ho's group developed and studied a series of CO₂-selective polymeric membranes containing sterically hindered polyamines [18][19][20]. They found that the steric hindrance effect of polyamines could significantly promote CO₂ transport performance in both CO₂ permeability and CO₂/gas (gas = H₂, N₂) selectivity, and this trend was more distinct in the case of moderately hindered polyamines (see **Figure 2**) [18]. Unfortunately, only a very limited number of systematic studies providing simultaneous CO₂ adsorption and diffusion/desorption kinetic properties have been devoted to amine-functionalized, silica-based membranes. Given this, in the earlier studies, the researchers developed a series of amine-containing organosilica membranes including unhindered (PA-Si, SA-Si) and sterically hindered (TA-Si, BTPP) amines, as well as a quaternary ammonium salt (QA-Si), and investigated the effect that amine type exerted on the CO₂ adsorption/desorption properties of solid powders and the related membrane performance (see **Figure 3**) [21][22][23][24]. It seems really important to more systematically compare the CO₂ separation performance of amine-functionalized silica-based membranes, despite many review papers for CO₂ separation membranes in the literature, which mostly review hydrocarbon-based membranes [4][25].

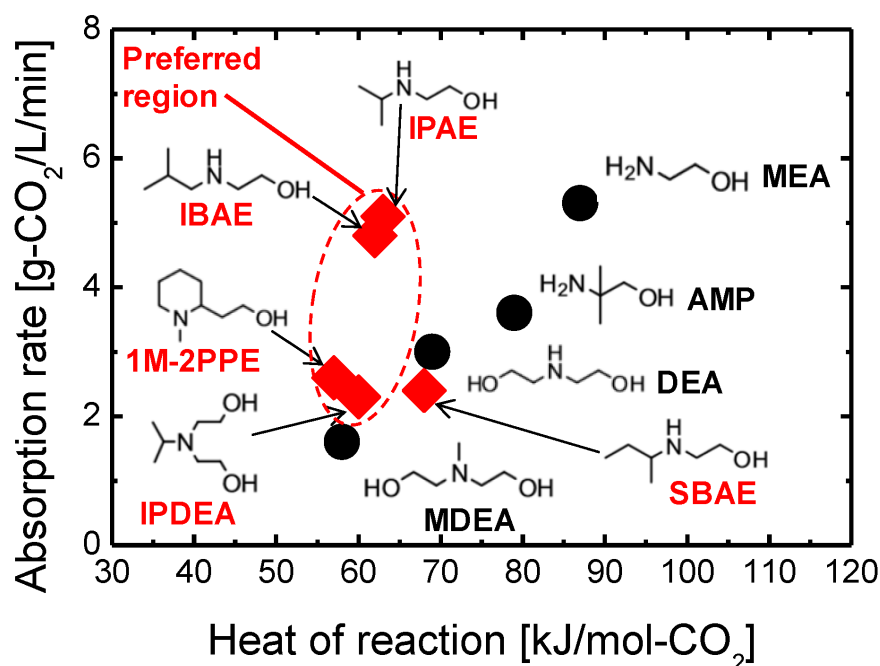


Figure 1. Relationships of absorption rate and heat of reaction between conventional and synthesized amines employed for CO₂ absorbents. Solid circles (●): conventional amines with no/low steric hindrance. Solid diamond (◆): synthesized amines with steric hindrance. Abbreviations: **MEA**, 2-aminoethanol; **AMP**, 2-amino-2-methyl-1-propanol; **DEA**, diethanolamine; **MDEA**, methyldiethanolamine; **IPAE**, 2-(isopropylamino)ethanol; **IBAE**, 2-(isobutylamino)ethanol; **SBAE**, 2-(secondarybutylamino)ethanol; **IPDEA**, 2-(isopropyl)diethanolamine; **1M-2PPE**, 1-Methyl-2-piperidineethanol. Generally, there is a trade-off relationship between the heat of reaction and the absorption rate for conventional amines. However, the introduction of steric hindrance creates a unique performance that features a low heat of reaction but results in a moderately high absorption rate. The data were adapted from ref. [15].

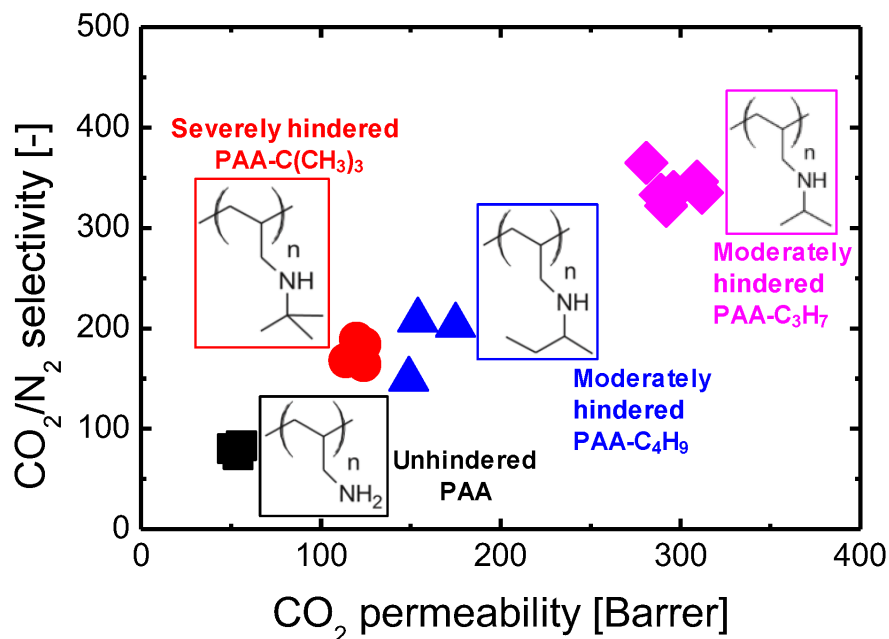


Figure 2. CO₂ separation performance comparison regarding the steric hindrance effect of polyamines for polyallylamine (PAA) membranes. CO₂/N₂ separation was performed at 110 °C and a feed pressure of 2 bar with water injection rates = 0.03/0.03 cm³/min (feed/sweep) using a feed gas composition of 20% CO₂, 40% H₂, and 40% N₂ (on dry basis). The data was adapted from ref. [18].

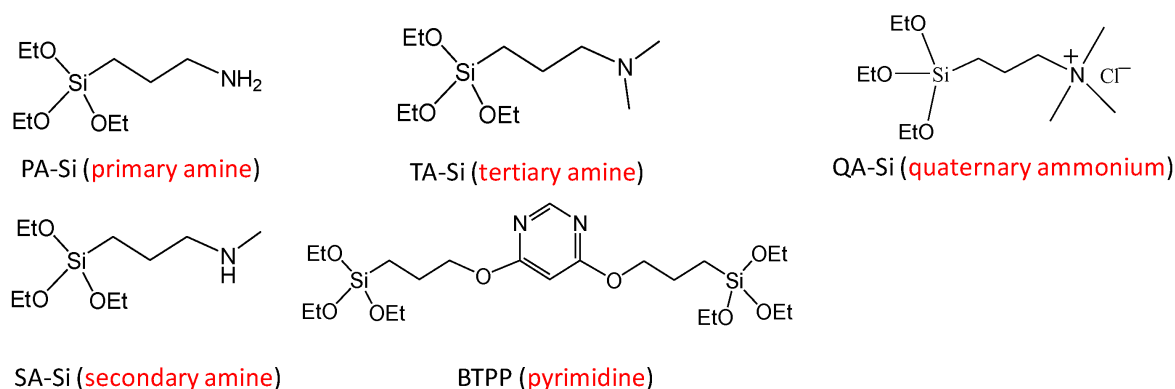
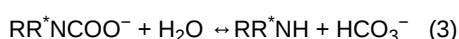
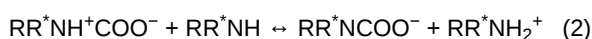


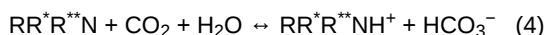
Figure 3. Chemical structures of amine-containing organosilica precursors employed in Prof. Tsuru's group.

2. Classifications and Reaction Activities between CO₂ and Amines

Amines are typically sub-classified as primary, secondary, or tertiary based on the degree of hydrocarbon substitution, while they also can be sub-classified as aliphatic, cycloaliphatic, aromatic, or heterocyclic. The diverse structures of amines confer basicity and a reaction activity that varies with acidic molecules (e.g., CO₂, H₂S). Generally, there are three factors that influence amine basicity: alkyl group substitution (including solvation effects and steric hindrance), resonance effect, and hybridization effect. The interlaced influences complicate the actual situation and make it more difficult to predict the down-to-earth basicity (or even the basicity order), which, however, can be reflected by the actual measurement of *pK_a*. Consequently, the normal aliphatic amines of primary, secondary and tertiary types are all of approximately equal basicity, which is generally stronger than aromatic amines. Notwithstanding, it is the steric hindrance effect rather than amine basicity that plays a key role in impacting their reaction activities with CO₂. Usually, a normal aliphatic primary or secondary amine can form a zwitterion upon encountering a CO₂ molecule (Equation (1)) and can then proceed with the formation of a fairly stable carbamate complex with another amine group (Equation (2)). Under humid conditions, this carbamate complex can further react with a water molecule and form a bicarbonate ion and a free amine group (Equation (3)) [26].



In Equations (1) to (3), R^* represents a H atom for a primary amine or another alkyl group. Equation (1) is a nucleophilic addition reaction, which is the rate-limiting process regardless of whether water is involved. Equations (2) and (3), however, represent rapid proton transfer reactions [27]. Tertiary amines, sterically hindered or not, on the other hand, owing to the lack of free hydrogen atom, are unable to react directly with CO_2 to form a carbamate. Instead, an alternative reaction occurs preferably to form a bicarbonate ion under humid conditions (Equation (4)) [28].



where R , R^* and R^{**} could be either different or identical alkyl groups.

Sterically hindered amines (SHAs), as originally defined by Sartori and Savage, can be identified from either of the following: (i) a primary amine in which the amino group is attached to a tertiary carbon atom or (ii) a secondary amine in which the amino group is attached to at least one secondary or tertiary carbon atom [29]. Based on this definition, it is difficult to identify tertiary amines with small bulkiness. Herein, the researchers regard tertiary amines as SHAs due to their similar performance. Unlike unhindered amines, SHAs are characterized by the formation of carbamates with intermediate-to-low stability due to the bulkiness of the substitutions attached to the amino groups. In this way, SHAs may provide a faster reaction with CO_2 while they lower the heat of reaction. As such, membranes with SHAs might proceed with CO_2 transport (adsorption-hop-desorption) more effectively across the membrane thickness. In addition, as shown in Equations (3) and (4), humidity or water vapor is also an important factor that impacts the CO_2 transport behaviors within amine-containing membranes, which might make it more complicated to investigate the role of amine type in CO_2 transport behaviors. The effect of humidity on CO_2 transport behaviors was therefore excluded here.

3. Synthesis of Amine-Functionalized Silica/Organosilica Membranes

In general, amine-functionalized silica-based membranes are mainly fabricated via either (i) direct sol-gel processing from amine-functionalized silica precursors [6][7][30] or (ii) post-grafting or impregnation of mesoporous silica membranes [11][12][13]. In addition, the chemical vapor deposition (CVD) method is also sometimes used for the direct deposition of amine-functionalized silica precursor on the substrates, which suggests advantages to prepare defect-free membranes compared with the sol-gel route [10]. However, this method consists of a thermal decomposition step for the silica precursor at higher temperatures (generally $> 400^\circ C$) prior to the deposition process, which could result in the degradation of most amine groups.

4. Role of Amine Type in CO_2 Separation Performance

As mentioned above, this research pays special attention to surveys of the role of amine type in CO_2 transport behaviors through amine-functionalized silica-based membranes. Generally, CO_2 transport through a membrane involves adsorption in the membrane surface or pore walls, diffusion across the membrane thickness, and desorption from the membrane permeate side (see **Figure 4a**). All the processes to some extent can be affected by the materials' chemistry, while the diffusion process can be generally governed by both the materials' chemistry and the membrane microstructure (e.g., pore size, pore length, and porosity) (see **Figure 4b**). Therefore, to systematically investigate the role of amine type in CO_2 separation performance through a membrane, both materials' chemistry in terms of CO_2 adsorption/desorption properties and membrane microstructure should be involved simultaneously.

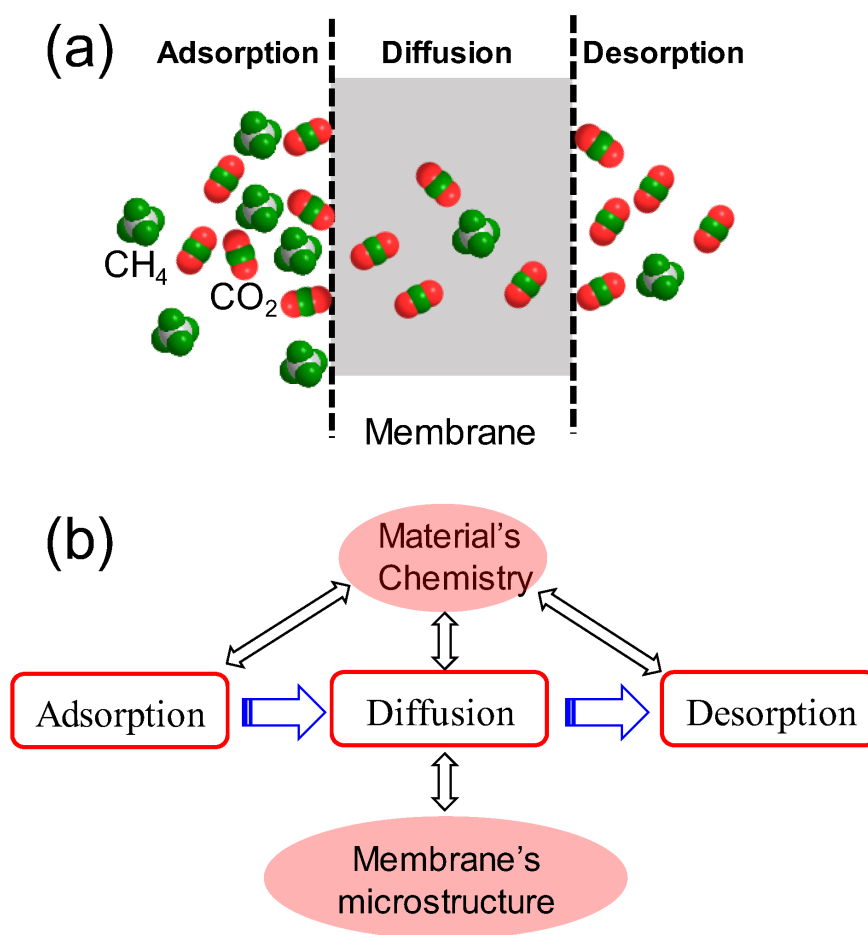


Figure 4. Schemes of (a) CO₂ separation through a membrane and (b) the factors impacting CO₂ transport behaviors including adsorption on the membrane surface, diffusion across the membrane thickness, and desorption from the membrane permeate surface.

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