

Review Article

Functionalized Mesoporous Silica Membranes for CO₂ Separation Applications

**Hyung-Ju Kim, Hee-Chul Yang, Dong-Yong Chung, In-Hwan Yang,
Yun Jung Choi, and Jei-kwon Moon**

Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon 305-353, Republic of Korea

Correspondence should be addressed to Hyung-Ju Kim; hyungjukim@kaeri.re.kr

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Mesoporous silica molecular sieves are emerging candidates for a number of potential applications involving adsorption and molecular transport due to their large surface areas, high pore volumes, and tunable pore sizes. Recently, several research groups have investigated the potential of functionalized mesoporous silica molecular sieves as advanced materials in separation devices, such as membranes. In particular, mesoporous silica with a two- or three-dimensional pore structure is one of the most promising types of molecular sieve materials for gas separation membranes. However, several important challenges must first be addressed regarding the successful fabrication of mesoporous silica membranes. First, a novel, high throughput process for the fabrication of continuous and defect-free mesoporous silica membranes is required. Second, functionalization of mesopores on membranes is desirable in order to impart selective properties. Finally, the separation characteristics and performance of functionalized mesoporous silica membranes must be further investigated. Herein, the synthesis, characterization, and applications of mesoporous silica membranes and functionalized mesoporous silica membranes are reviewed with a focus on CO₂ separation.

1. Introduction

To overcome the increasing challenges posed by the need for new energy sources and environmental protection, advanced molecular separation and purification technologies are required. Absorption [1], adsorption [2, 3], membrane separation [4], and capture [5] technologies are currently available to address these challenges. Among them, membrane-based separations are becoming increasingly relevant for a number of applications due to their low energy requirements and steady-state operations [6–9]. Membrane-based separation is applicable not only to liquids but also to gases. Membranes are widely used in desalination industry and for other industrial purposes such as wastewater treatment [10] and recovery of valuable organic matter [11]. Membrane separation can be further classified into pervaporation [12], microfiltration, ultrafiltration [13], nanofiltration [14], reverse osmosis [15], and forward osmosis [15] depending on the manner of membrane operation and its pore range. In gas separation, natural gas sweetening, that is, removal of CO₂ and H₂S from

hydrocarbons [16], and CO₂ separation in a coal-fired power plant [17] are the most important processes. Additionally, membrane separation is used to induce separation between electrodes in battery-related applications [18].

With the large specific surface areas, high pore volumes, tunable pore sizes, and stability, mesoporous silica is a decent candidate as membrane material for separation applications [19]. Its uniform pore structures and high silanol group densities also make it attractive for separation and purification applications [20]. Silanol groups are important for using silica as versatile support after modification.

Mesoporous materials are typically formed using a micelle-templating process, following either an electrostatically driven cooperative assembly pathway or a nonionic route in the presence of uncharged surfactants as structure-directing agents. M41S was the first reported ordered mesoporous silica material [21]. Emerging applications in catalysis, adsorption, and separation have boosted the development of many other ordered mesoporous silica materials, such as the SBA-n [22, 23], Fudan University Material (FDU) [24],

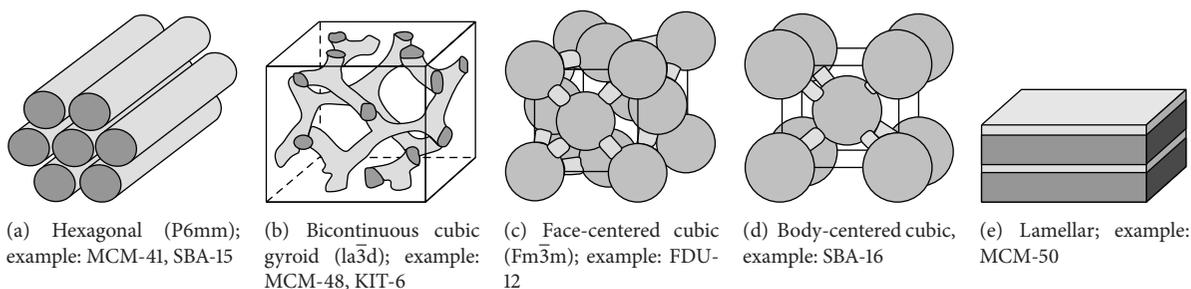


FIGURE 1: Structures of various ordered mesoporous materials [27].

Korea Advanced Institute of Science and Technology (KIT) [25], and anionic-surfactant-templated mesoporous silica (AMS) [26] families. Many of these mesoporous materials (see Figure 1) have been explored for separation applications [27].

A number of studies on the adsorption uptake of acidic gases such as CO_2 by mesoporous silica molecular sieves have been reported [27, 28]. Mesoporous silica, such as SBA-15 [29], MCM-41 [30], and MCM-48 [31], were shown to be good supports for separation membranes, offering selectivity over other gases such as CH_4 and N_2 . Since gas separation is derived from transport phenomena and mesostructures are a framework of gas transport, a 3D structure with interconnected pores is highly preferred to overcome the limitation of diffusion. Modification of these molecular sieves with organic groups is required to tailor their specific sorption capacities [32]. Thus, effective methods for the fabrication of mesoporous silica membranes and their functionalization with appropriate modification agents are crucial for advancing their practical application. Herein, amine-functionalized mesoporous silica membranes and their use for CO_2 gas separation are discussed.

2. Functionalized Silica Membranes

2.1. Mesoporous Silica Membranes. Adapting mesoporous silica molecular sieve powders to a membrane configuration while preserving their adsorptive properties presents an attractive but challenging possibility for developing separation processes. For instance, mesoporous silica in a membrane configuration allows gas separation under steady-state conditions, wherein selective adsorption occurs on the feed side, followed by selective diffusion across the membrane with continuous desorption on the permeate side. Specifically for CO_2 separation, the CO_2 molecules are chemisorbed on the active layer of the membrane (in the pores), diffused through the pores of the membrane, and then desorbed from the other side of the membrane [27]. At the same time, other gases are retained by the membrane layer. Figure 2 shows a schematic of such transport at the molecular level. Because mesoporous silica molecular sieves do not have mechanical strength, various macroporous supports, including ceramics and polymers, are necessary. These support materials do not function as barriers; only the mesoporous silica membrane layer acts as a bottleneck for the transport process. Thus,

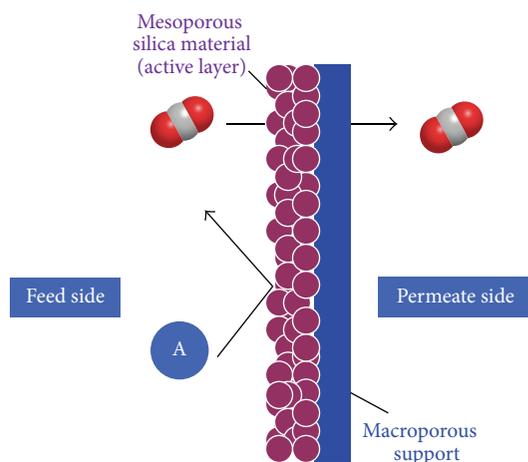


FIGURE 2: Schematic of transport at the molecular level through a supported asymmetric mesoporous silica membrane. CO_2 is the permeating gas, and A is the retentate gas molecule.

mesoporous materials in the form of thin films on supports (asymmetric membranes) may offer a number of advantages in many emerging applications [33]. Such membranes act as barriers to the mass transfer between phases, allowing the separation of the phases under a driving force. Previously, thin layers of mesoporous silica membranes have been grown on ceramic supports such as α -alumina [34, 35] to increase their mechanical stability [36]. Both disk and tubular configurations are possible. However, compared with the formation of disk-type membranes, the deposition of mesoporous silica membranes on tubular α -alumina supports is challenging due to the nucleation and growth behavior that occurs on curved surfaces. On the other hand, the tubular form guarantees a high packing density with a large surface area. Recently, mesoporous silica membranes were successfully synthesized on polymeric hollow fiber supports for more versatile applications. It is possible to fabricate much thinner (μm level) polymeric hollow fibers than tubular ceramic supports (mm level), and thus significantly higher packing densities and larger surface areas per module can be achieved. In addition, polymer-based supports are generally cheaper than ceramic materials and highly reproducible. One disadvantage of polymeric supports compared with ceramic supports is their limited thermal stability, which prevents

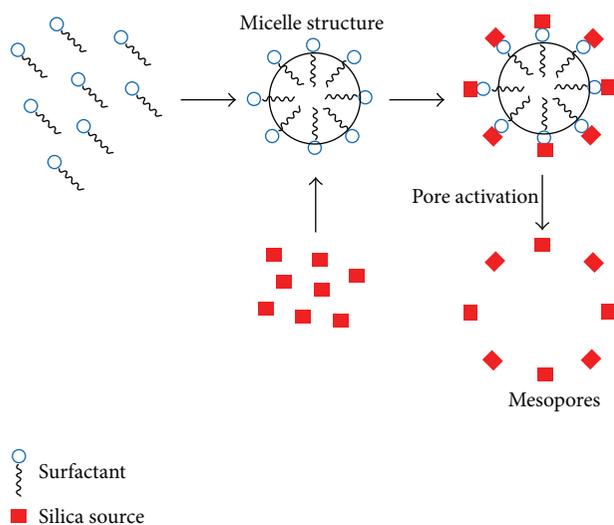


FIGURE 3: Mechanism for the synthesis of mesoporous silica in the presence of a cationic surfactant.

the use of high-temperature surfactant removal processes, particularly calcination. Thus, there are pros and cons for each type of support that must be considered when selecting the appropriate support material for a specific application.

Supported mesoporous silica membranes with controlled structures, like silica powder, are synthesized via the well-established sol-gel method but in the presence of support materials. This technique involves hydrolysis and condensation of respective precursors to form colloidal sols [27]. Figure 3 shows the mechanism for the synthesis of mesoporous silica in the presence of a cationic surfactant. When dissolved in water, the cationic surfactant forms micelle structures. In this process, the cationic “heads” of the surfactant molecules are arranged to the outer side, while their hydrophobic “tails” collect in the center of each micelle. The silica source then covers the micelle surfaces. Once the surfactant is removed via calcination or extraction, the pores are activated.

Pretreatment of the supports using several different methods has been attempted to improve the quality of the membranes. Polishing of ceramic supports provides even surfaces that afford more reproducible membranes. Seed layer deposition has also been shown to result in smoother surfaces and increase the chance of nucleation that influences membrane growth.

Synthesized mesoporous silica membranes can be characterized using various techniques. The most important property of membranes is a defect-free and continuous layer. To monitor the top surfaces and cross sections of membranes, scanning electron microscopy (SEM) is employed. Accurate determination of the membrane thickness, which is an important variable for calculating the gas permeability, is obtained via SEM coupled with energy-dispersive X-ray spectroscopy (EDS) (see Figure 4). To avoid rupture of the silica layer and silica/support interface, treatment with liquid nitrogen is generally performed first to preserve the membrane layer for proper observation. Unlike mesoporous silica

powders, however, other properties of mesoporous silica membranes are not easily characterized and investigated. Thus, numerous efforts are underway to obtain the same information that can be gathered for silica powders. For instance, N_2 physisorption analysis is used to directly investigate the pore structure of silica powders, but this technique is quite limited for supported mesoporous silica membranes due to the presence of the support and the small quantity of membrane. As an alternative, a nondestructive, reusable N_2 physisorption method was developed as a lab-made apparatus for supported inorganic membranes [37]. This method was used to determine the direct pore structure of supported mesoporous silica membranes, and the results were compared with those obtained for powder samples of zeolite [38] and mesoporous silica [39] membranes. Depending on the thickness of membrane, this method requires around 10 consistent membranes. If the membranes are varied, obtained data have low reliability. To reduce the needed sample quantity and other artifacts, a more advanced technique is required for future research.

2.2. Functionalization of Mesoporous Silica Membranes. The typical pore sizes (2 to 50 nm) of mesoporous silica membranes preclude direct application in molecular separations involving small and light gases. Thus, to impart highly selective properties to these membranes, further modification of the mesopores is necessary. Conventional CO_2 capture technology uses aqueous amines to absorb CO_2 , but this conventional method has several disadvantages in terms of regeneration, energy consumption, and so forth. In addition, the conventional method is only cost effective for concentrated streams of CO_2 . As an alternative benchmark technology for aqueous amine absorption, amine-functionalized mesoporous silica powder materials, such as MCM-41 [40] and SBA-15 [41] with high concentrations of amine groups inside their pores, have been shown to exhibit unusually high CO_2 sorption capacities. This selectivity is attributed to both the presence of amines on the surfaces of the powder particles and the high loading of amine groups in the mesopores following functionalization. Based on the above concept, the fabrication of amine-functionalized mesoporous silica in a membrane configuration has long been of interest for CO_2 separation. Amine-functionalized membranes should provide steady-state operation, be easy to regenerate and energy efficient, and enable the capture CO_2 from dilute streams.

There are three major techniques for the functionalization of mesopores: cocondensation, impregnation, and postsynthesis grafting, as shown in Figure 5. Impregnation involves loading a large quantity of amines dissolved in a solvent inside the pores (Figure 5(a)). However, the loaded amines tend to conglomerate, and these agglomerates are not stable after several adsorption/desorption cycles or under pressurized gas flow. During cocondensation, the amine groups are covalently bonded to the silica matrix (Figure 5(b)) and a certain percentage of the Si atoms are replaced by amino-silane groups. This method results in the uniform distribution of various functional groups without pore blocking. In

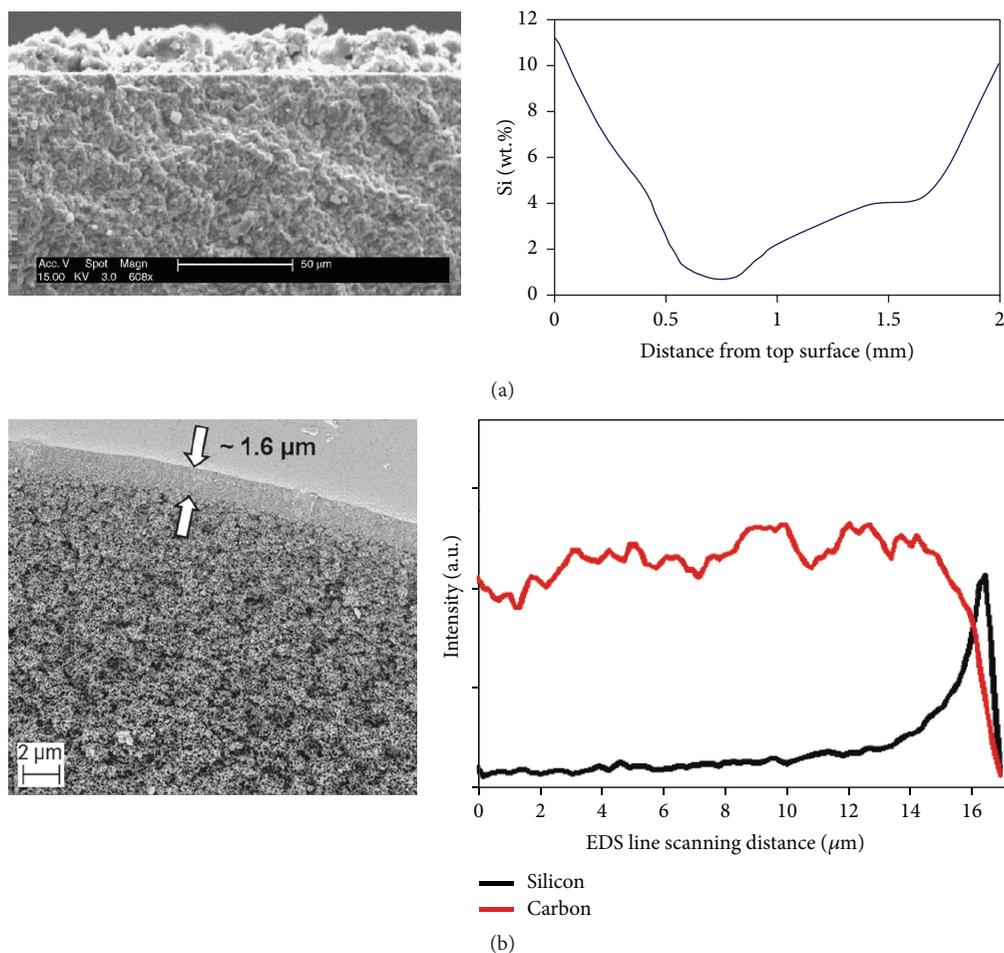


FIGURE 4: SEM images coupled with EDS line scanning analyses for (a) a flat MCM-48 membrane on an α -alumina support [52] and (b) worm-like mesoporous silica membrane on a polymeric hollow fiber support [42].

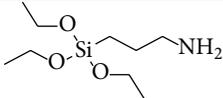
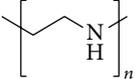
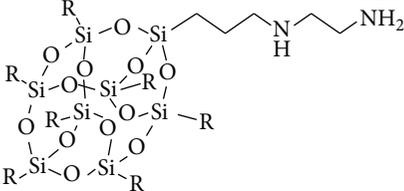
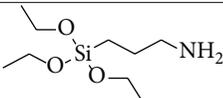
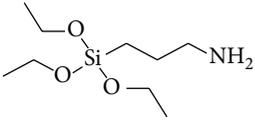
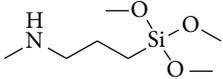
postsynthesis grafting, a reaction occurs between the silanol groups of the silica and the amines (Figure 5(c)). This approach maintains the substrate structure, and the formed amino oxides remain stable, even after several adsorption/desorption cycles.

There have been numerous studies of the amine functionalization of mesoporous silica membranes [42–48]. Table 1 lists reported examples of mesoporous silica membranes that have been functionalized with amine groups for CO_2 separation. Various supports, mesoporous silicas, functionalization agents, and methods have been used till date. Because CO_2 separation is governed by a gas diffusion mechanism, mesoporous silica containing three-dimensional interconnected pore structures, with MCM-48 as a good representative material, is most often selected by researchers to avoid the consideration of the deposition direction. The common supports used to impart mechanical strength to the mesoporous silica layer include ceramics, alumina, and more recently polymers. As mentioned above, the preferred pore activation process (thermal calcination or solvent extraction) is highly dependent on the support material. For amine modification, postsynthesis grafting provides more stable

amino-oxide hybrid membranes than other techniques. In addition, because it is important to be able to correlate pore structures, presumably the monolayer of the amine group, to transport phenomena, postsynthesis grafting is the preferred functionalization method. Amine groups are selected based on not only their affinities and reactivity with the silanol groups on the mesoporous silica but also their ability to capture CO_2 , which is typically estimated from their performance when adsorbed on silica powder.

2.3. Characterization of Functionalized Mesoporous Silica Membranes. Verification of the functionalization of mesoporous silica membranes is another challenging step. Characterization of amine-functionalized mesoporous silica powders involves the determination of their amine loading, bonding properties, and CO_2 capture capacities [49]. The ability to characterize amine-functionalized membranes is, as described above, somewhat limited, but it is possible to use similar approaches. SEM observation to confirm that the membrane remains intact and the support and silica structure have not collapsed following incorporation of the

TABLE I: Published mesoporous silica membranes functionalized with amine groups for CO₂ separation.

Support	Mesoporous silica	Functionalization agent	Functionalization method	Ref.
Alumina disk	MCM-48		Postsynthesis grafting	[47]
α -Alumina disk	MCM-48		Postsynthesis grafting	[43]
Polymeric hollow fiber	Worm-like mesoporous silica	 R = <i>i</i> -butyl	Impregnation	[42]
Vycor tube	Vycor tube		Postsynthesis grafting	[46]
Polymeric hollow fiber	Worm-like mesoporous silica		Postsynthesis grafting	[48]
γ -Alumina disk	Hybrid silica	 	Cocondensation	[44]

amine groups is generally a prerequisite prior to quantitative analysis (Figures 6(a)-6(b)).

Amine loading can be directly determined via thermogravimetric analysis, as is the case for silica powders, but obtaining the required sample quantity is often unrealistic considering the thinness of membrane layers. Thus, amine loading is typically calculated indirectly by comparing the gas permeation properties of nonfunctionalized and amine-functionalized membranes. A significant decrease in the permeability of different gases indirectly indicates the loading of amine groups in the pores.

For silica powders, it is also easy to obtain information on the bonding between silanol and amine groups using various spectroscopic techniques (Fourier transform-infrared (FT-IR), Raman, ultraviolet-visible, etc.) and the quantity of adsorbed CO₂ after CO₂ capture. However, once again the limited sample quantity for supported mesoporous silica membranes makes the use of these methods unrealistic. Thus, most efforts focus on characterization of the membrane surface. FT-IR/attenuated total reflectance (ATR) spectroscopy is one of the most reliable tools for this analysis (Figure 6(c)). X-ray diffraction (XRD) analysis has also been proved to be a useful method. In Figure 6(d), it can be seen that the

peaks in the XRD pattern of a polyethylenimine- (PEI-) modified MCM-48 membrane are blunter and lower in intensity than those for a bare MCM-48 membrane. This result indicates that the contrast between the pores and pore walls was reduced following amine functionalization and thus suggests that the mesoporous silica membrane was properly functionalized.

The CO₂ capture capacity is reflected by the selectivity of the membrane during the separation process. Gas permeation tests (single or mixed gases) are used to evaluate the membrane separation performance. As described above, a significant drop in permeability occurs following the pore modification. Moreover, the selectivity (ratio of the permeabilities of different gases) is tailored according to the choice of amine functional groups.

2.4. CO₂ Separation Using Mesoporous Silica Membranes. The permeability (P_A) of a membrane to a gas molecule A is

$$P_A \equiv \frac{N_A l}{p_2 - p_1}, \quad (1)$$

where N_A is the steady-state flux of the gas through the membrane, l is the membrane thickness, and p_2 and p_1 are

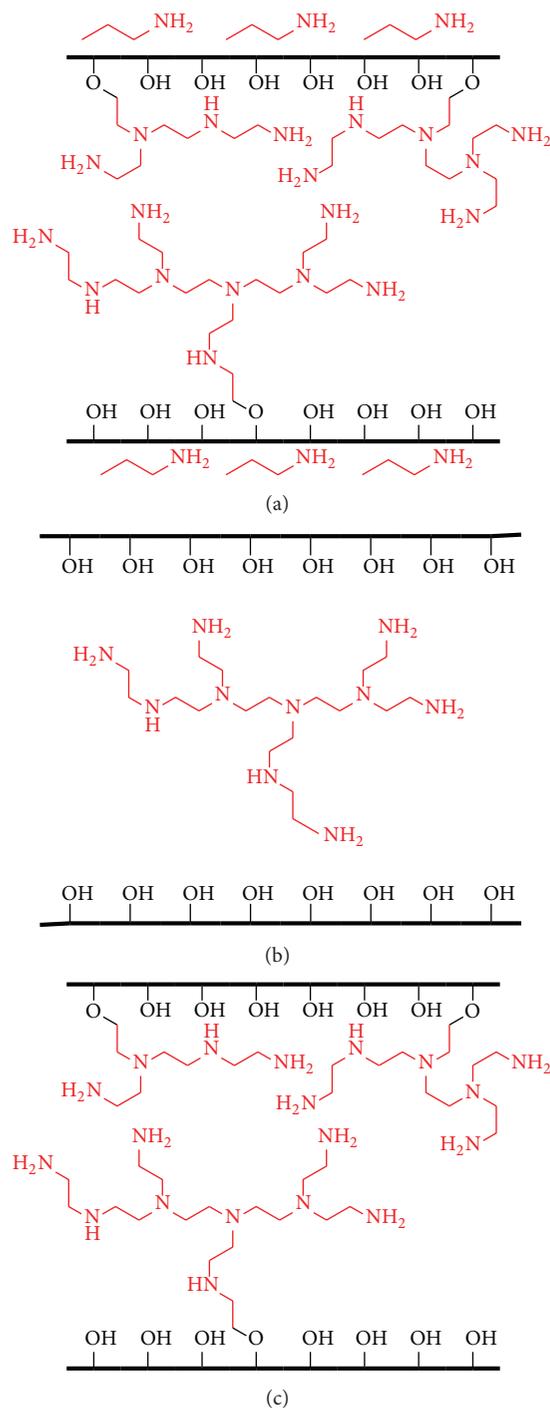


FIGURE 5: Porous silica pores loaded with polyethylenimine (PEI) using three different loading techniques: (a) cocondensation, (b) impregnation, and (c) postsynthesis grafting.

the upstream and downstream partial pressures of gas A , respectively. When the diffusion process obeys Fick's law and the downstream pressure is much less than the upstream pressure, the permeability is given by

$$P_A = D_A S_A, \quad (2)$$

where D_A is the average effective diffusivity through the membrane and S_A is the apparent sorption coefficient caused by the silica surface or the amine groups.

The ideal selectivity of a membrane for gas A over gas B is hence the ratio of their gas permeabilities:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left[\frac{D_A}{D_B} \right] \left[\frac{S_A}{S_B} \right], \quad (3)$$

where D_A/D_B is the diffusivity selectivity, that is, the ratio of the diffusion coefficients of gases A and B . The ratio of the solubilities of gases A and B , S_A/S_B , is the solubility selectivity. The diffusivity selectivity is strongly influenced by the difference in sizes of the penetrant molecules and the size-sieving ability of the membrane material, whereas the solubility selectivity is controlled by the relative adsorption/thermodynamic affinities of the penetrants for the membrane matrix [50]. An interesting aspect of amine-functionalized mesoporous silica membranes is that both types of selectivities can potentially be controlled as a result of the membrane modification.

Figure 7 shows the mechanism for CO_2 adsorption on amine-oxide surface, which is facilitated by the transport of CO_2 molecules. Unlike most other gas molecules, CO_2 reacts with amine groups via an acid-base reaction. Specifically, two moles of the amine group reacts with one mole of CO_2 to form a carbamate. The pressure of the gas flow then causes the CO_2 molecules to hop along the surface via adsorption on the next set of two amine groups. This surface diffusion contributes to the CO_2 flow and results in the CO_2 molecules passing more rapidly through the membrane than other gases, and it is the source of the selectivity for CO_2 . Notably, when water is present, the effect of surface diffusion is greater because only one mole of the surface amine is needed to react with one mole of CO_2 by forming ammonium bicarbonate, leading to an even more rapid flow of CO_2 through the membrane and thus higher selectivity. Consequently, each single reaction aids in the smooth flow of a CO_2 molecule via facilitated transport. It should also be noted that the temperature and feed pressure affect the rate of desorption of CO_2 molecules from the amine groups, and the feed ratio and CO_2 concentration in the feed affect the competitive transport of different gases.

Table 2 lists the important parameters for the CO_2 separation performance of reported amine-functionalized mesoporous silica membranes. Excellent membrane performance requires both high selectivity and high CO_2 permeance, as described by Robeson [51]. However, there is a trade-off between the two, as can be seen in Table 2. A high loading of amine groups provides very high selectivity but results in low permeance values. On the other hand, high CO_2 permeance properties with low amine loading levels result in very low selectivities. In addition, Kumar and Kim reported reverse selective properties wherein CO_2 molecules were trapped and passed more slowly through the membrane than other gases when amine groups with very high affinities for CO_2 were used [43, 48]. In these cases, due to the strong affinities of the amine groups, cross-linking occurred and resulted in sticky diffusion of the CO_2 . Amine-cross-linking occurs when ammonium carbamates are formed because two

TABLE 2: Performance of published amine-functionalized mesoporous silica membranes for CO₂ separation (GPU = 3.35 × 10⁻¹⁰ mol m⁻² s⁻¹ Pa⁻¹).

CO ₂ permeance (GPU)	Selectivity (CO ₂ /N ₂ or CH ₄)	Presence of water	Temperature	Ref.
3	800	X	373 K	[47]
0.144	0.012	O	294 K	[43]
100	17	X	308 K	[42]
0.8	10	X	393 K	[46]
1.8	0.15	X	308 K	[48]
9.4	2.5	O	308 K	[48]
63	4	X	393 K	[44]

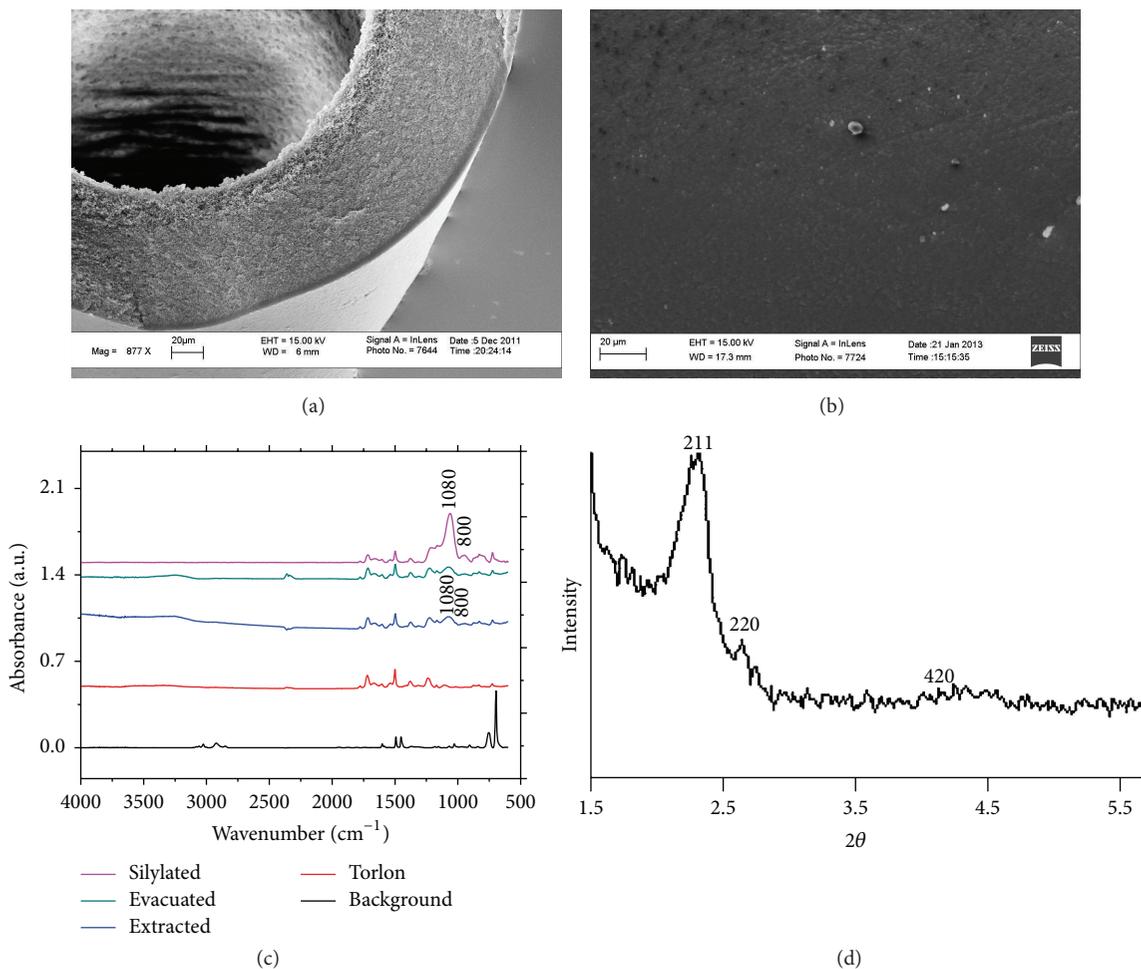


FIGURE 6: Characterization of modified mesoporous silica membranes. SEM images of the (a) cross section and (b) top view of an aziridine-functionalized mesoporous silica membrane [48], (c) FT-IR/ATR spectra for a silylated mesoporous silica membrane [53], and (d) XRD pattern of a PEI-modified MCM-48 membrane [43].

amine groups sterically exist very close. Thus, appropriate mesoporous materials, functionalization agents, and modification techniques must be employed when developing CO₂ separation membranes. On the other hand, because a wide range of amine-functionalized mesoporous silica membranes are available today, there is significant potential for fabricating highly tailored, and therefore very selective, membranes for CO₂ separation.

3. Summary

Membrane-based separation of CO₂ from mixed gas flows represents a rapidly growing research field for the porous materials community. Amine-functionalized mesoporous membranes show significantly promising CO₂ separation due to the strong adsorption properties of the surface amine groups and the regular mesopore structure used to support

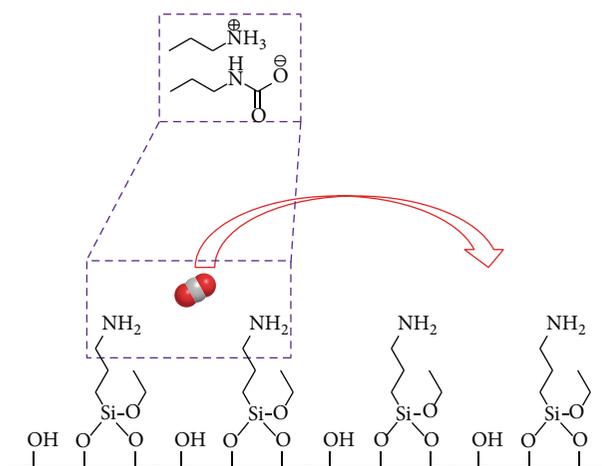


FIGURE 7: Mechanism of CO₂ adsorption on an amine-oxide surface and facilitated transport of a CO₂ molecule.

them. However, because the synthesis and characterization of amine-functionalized mesoporous silica membranes are complex, much is not yet known regarding amine loading levels, membrane pore structures, gas permeation mechanisms and their kinetics, and the correlations between these properties. Based on results obtained to date, it is thought that, along with polymers, zeolites, metal organic frameworks, and mixed-matrix membranes, amine-functionalized mesoporous silica membranes represent a technologically scalable platform. This review briefly discusses the efforts to synthesize mesoporous silica membranes, functionalize them with amines, characterize the functionalized membranes, and study their performance in CO₂ separation applications.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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