Zeolite-based catalytic membrane reactors for thermo-catalytic conversion of CO₂

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SUMMARY
Zeolite-based catalytic membrane reactors have been successfully applied in overcoming the thermodynamic limitations of CO₂ hydrogenations and dry reforming of methane (DRM) reactions. This review summarizes the zeolites as membrane reactor components regarding the permeance, permselectivity, durability, conversion, selectivity, and stability by referring to the synergy of catalyst and membrane. Also, five operation parameters (temperature, pressure, feed ratio, sweeping gas flow rate, and gas hourly space velocity) are introduced regarding their impacts on the performance of membrane reactor. Besides, synthesis methods and conditions for zeolite membranes are critically illustrated in the category. Moreover, representative surface and structure properties of zeolite membranes are discussed by relating to the synthesis-structure-performance relationships. Finally, conclusive remarks are demonstrated and possible solutions to existing challenges are proposed. So far, this is the first time to discuss the applications of zeolite membrane reactors in the CO₂ adsorption, separation, activation, and conversion in reforming and hydrogenation processes.

INTRODUCTION
With rapid industrialization and booming human activities, the consumption of fossil fuels results in the excessive amount of CO₂ released into the atmosphere, which causes the greenhouse effect and subsequent environmental problems. Therefore, it is imminent to develop a highly efficient material and process to adsorb, separate and convert CO₂ (Yeo et al., 2013; Vinoba et al., 2017; Waheed et al., 2018; Harrould-Kolieb, 2019). Physically, CO₂ can be captured via wet scrubbing (Muchan et al., 2017), distillation (Yousef et al., 2018), pressure swing adsorption (PSA) (Riboldi and Bolland, 2017), and temperature/vacuum swing adsorption (TVSA) (Jiang et al., 2020). Compared with the above processes, membranes enjoy a few advantages for gas separations, such as continuous operation, cleanliness, high reliability, low cost, high energy efficiency, and flexibility (Yeo et al., 2013; Vinoba et al., 2017; Jahan et al., 2018; Li et al., 2010, 2012, 2021b; Kathiraser et al., 2013a, 2013b; Chen et al., 2019, 2020a; Xu et al., 2021; Wenten et al., 2021; Wang et al., 2018). Apart from the physical separation, CO₂ conversion to value-added chemicals (e.g., syngas and methanol) has drawn increasing attention, including photo-, electro-, and thermo-catalytic processes (Dewangan et al., 2020; Das et al., 2020b; Shoji et al., 2020; Zhou et al., 2020a, 2020b). In photo-catalysis, renewable solar energy can be used to drive the low-temperature reaction. In electro-catalysis, catalytic stability will be prolonged and energy consumption will be saved since high-temperature condition is avoided. However, the poor conversion rate and product selectivity in photo- and electro-catalysis restrict their large-scale application in the industry (Sakine et al., 2016; Kulandaivalu et al., 2020). In comparison, featured with the satisfactory catalytic performances of CO₂ transformations, thermo-catalysis is more competitive, mainly including hydrogenations (Ashok et al., 2017, 2020a; Ashok et al., 2020b; Bian et al., 2020a; Dewangan et al., 2020; Hongmanorom et al., 2021b, 2021a; Pati et al., 2020; Yu et al., 2018a, 2018b; Poerjoto et al., 2021; Li et al., 2021a; Wai et al., 2021; Gao et al., 2022a, 2022b), reforming (Li et al., 2016, 2020; Bian et al., 2017, 2021, 2016, 2021; Bian and Kawi, 2017; Li and Kawi, 2018; Gao et al., 2020b, 2021b, 2021a, 2022a, 2022b; Kawi et al., 2015; Das et al., 2020a, 2020b, 2020c; Mo et al., 2014; Ashok et al., 2018; Kathiraser et al., 2013a, 2013b; Hu et al., 2020, 2021, 2020) and reversed water-gas shift reaction (Chen et al., 2020b; Liu et al., 2020a, 2020b, 2020b).

Based on the above discussions, it would be attractive if an integrated reactor system is constructed to form a synergy of physical and chemical processes. One of the representatives is the membrane catalytic reactor, which has been applied in environmental protections and exhaust gas conversions (Bian et al., 2020b;
Yang et al., 2013; Wang et al., 2020a, 2020b), such as CO oxidation (Medrano et al., 2018; Peng et al., 2019; Bernardo et al., 2008; Galletti et al., 2008), water-gas shift (Arvanitis et al., 2018; Tang et al., 2010; Kim et al., 2012, 2013a, 2013b; Wang et al., 2014; Zhang et al., 2012; Dong et al., 2015; Yin et al., 2019; Bang et al., 2021; Sun et al., 2020) and volatile organic compound (VOC) combustion (Liu et al., 2020c; Chen et al., 2014; Yan et al., 2014). Specifically, membrane catalytic reactors are also deemed as a promising candidate for the conversion of CO2 into value-added products. Despite several existing challenges, such as partial heat loss and selectivity issues at high temperatures (Iwakiri et al., 2022), the membrane catalytic reactors have drawn tremendous interest since the catalytic reaction can possibly overcome the thermodynamic limitation, thus exhibiting an improved conversion efficiency and product yield (Makertihiarta et al., 2017). Also, the separation of products could be simplified in membrane reactors, favoring a large-scale application with a low operation cost and complexity (Wenten et al., 2021). As for the membrane materials, polymers have been applied for CO2-involved reactions, such as Nafion®, polytetrafluoroethylene (PTFE), polyvinyl alcohol (PVA), and polyacrylic acid (PAA) (Struis et al., 1996; Ountaksinkul et al., 2019). However, polymers suffer from poor thermal stability and the trade-off between selectivity and permeability (Algieri et al., 2021). In comparison, inorganic materials like silica-alumina composites and zeolites are widely developed as an alternative (Diban et al., 2013a; Farsi and Jahanmiri, 2014). Featured with a higher permselectivity and structural stability than silica-alumina materials, zeolite membranes have been extensively applied for high-temperature thermo-catalytic conversion of CO2. Moreover, the superior chemical stability in harsh reaction conditions, abundant molecular-size pores, highly ordered crystalline structures, and low cost render zeolites the most attractive materials for membrane reactor preparations to enhance both selectivity and durability (Wenten et al., 2021). In terms of CO2 utilizations, two representative reactions are mostly studied using zeolite-based catalytic membrane reactors, that is, CO2 hydrogenation (Raso et al., 2021; Tavolaro and Tavolaro, 2017; Gorbe et al., 2018) and dry reforming of methane (DRM) (Bosko et al., 2010). In the last few years, however, relevant reviews are only focused on the following topics: zeolite catalysts for VOC removal (Feng et al., 2018), developments of specific zeolite structures (Rimaz et al., 2022; Collins et al., 2020; Li et al., 2021c; Xu et al., 2021) and zeolites membranes adopted in heterogeneous reactions (Wenten et al., 2021). Therefore, this review for the first time discusses the applications of zeolite membrane reactors in the CO2 adsorption, separation, activation, and conversion in reforming and hydrogenation processes, together with the impacts of operation conditions. Besides, to pave the way for a better understanding of the structure-performance relationship, the transport mechanisms of various molecules (e.g., H2, CO2, H2O) via zeolite membranes is illustrated in detail. Moreover, to provide information for a smarter design of zeolite membranes, the synthesis strategies and parameters are well discussed. Furthermore, to realize a CO2-rich raw feed through an efficient separation from the upstream, influential factors are introduced in terms of the structure and surface properties of zeolite membranes. Finally, conclusive remarks and future work directions are proposed.

**TRANSPORT MECHANISMS VIA ZEOLITE MEMBRANES**

When molecules pass through the inorganic membranes (e.g., zeolites), the transport behaviors mainly include four types, that is, Knudsen diffusion, surface diffusion, molecular sieving, and capillary condensation (Figure 1) (Liu et al., 2018a, 2018b). For example, when the pore size of the membrane is smaller than the mean free path dimensions of gas molecules, Knudsen diffusion occurs, where the collisions between molecules are dominant compared with the surface wall-molecule interaction. Also, in normal Knudsen diffusion, the flux is negligibly affected by the temperature (Zito et al., 2017). Differently, surface diffusion is largely determined by the adsorption behaviors of molecules on the zeolite surface. The more polar molecules prefer to adsorb first, limiting the transport of weakly adsorbed ones by reducing the available space. This kind of diffusion follows the molecular hopping between the adsorbed molecules, which usually takes place at low temperatures (Zito et al., 2017, 2018a). Rather than the polarity, the diffusion of molecules in molecular sieving is exclusively influenced by size. The smaller molecule is able to pass through the membrane while the larger ones are blocked. Instead of the size exclusion, in capillary condensation, selective diffusion through the porous solids is enabled when the saturation pressure is different among the molecules. In detail, when the pressure of gas vapor is lower than the saturation pressure, condensation takes place, which restricts the adsorption and transport of other competitors since the pore is blocked (Yeo et al., 2012).

In certain conditions, inter-transition of transport mechanisms might occur; meanwhile, the above diffusion regimes may also evolve into other behaviors (Yeo et al., 2012). For instance, the inter-transition between Knudsen diffusion and surface diffusion happens with different temperatures and molecule polarities. In
particular, H2 transport follows Knudsen diffusion regardless of the temperature due to the non-polarity and weak adsorption. While for the polar molecules (e.g., CO2 and H2O), surface diffusion is the main mechanism at low temperatures, which is shifted to Knudsen diffusion at high temperatures where the adsorption is weakened. On the other hand, when the pore geometry changes (e.g. pore diameter and tortuosity), Knudsen diffusion may be replaced by surface diffusion since the mobility of surface adsorbed molecules are limited (Zito et al., 2017; Caravella et al., 2016). In another case where Knudsen diffusion and gas translation diffusion are involved, the transition between these two modes relies heavily on the ratio of molecular size to pore size. Particularly, at a high temperature, the molecules maintain the gas state, and their movement is hindered by the comparable size to that of pores, indicating a gas translation model. However, when the kinetic diameter of molecule is much smaller than the pore diameter, Knudsen diffusion becomes dominant because of the nearly zero activation energy for diffusion (Zito et al., 2018b).

Figure 1. Scheme of transport mechanism via microporous membranes
(A) Knudsen diffusion; (B) Surface diffusion; (C) Molecular sieving; (D) Capillary condensation. Reproduced with permission from (Yeo et al., 2012). Copyright 2012, Elsevier.

SYNTHESIS OF ZEOLITE MEMBRANES

The catalytic performance of zeolite membrane reactors depends on the quality and physicochemical property, which are considerably affected by the preparation conditions, such as seed, pH, chemical ratio, duration, and temperature. Besides, the synthesis strategies exert a profound impact on membrane formation, including but not limited to template elimination, usage of gels, and organic structure-directing agents (OSDAs). In the following sections, both the parameters and methods will be discussed in terms of the relationships between the synthesis and property of zeolite membranes.

Preparation conditions

The growth process of zeolite crystals undergoes three phases—nucleation, dissolution, and recrystallization. Compared with the seedless strategy where the mother liquor is directly deposited, seeding still draws a wide attention because of the high concentration of nuclei and fast nucleation kinetics (Fasolin et al., 2019). The seeding process is determined by suspension concentration and seed size. When too many seeds are fed, the resulting particle agglomeration and multi-layers will increase the membrane thickness, which causes stress and defect (Karakiliç et al., 2019; Meshkat et al., 2018). On the other hand, boundary gaps may be formed when insufficient amounts of seeds are unable to fully cover the support surface (Karakiliç et al., 2019). In addition to the seed concentration, the seed size is crucial to the membrane quality. A large seed size follows the secondary growth route, resulting in poor crystal intergrowth and rough zeolite surface. Also, the low steric hindrance leads to a random growth of the seeds (Mirfendereski and Mazaheri, 2021). However, a large crystal strengthens the support-zeolite interaction and enhances the
diffusivity (Mirfendereski, 2019). On the contrary, a small seed size is favored since the intercrystalline gaps are reduced, producing a homogeneous structure. Moreover, the formed zeolite membrane layer tends to possess a strong orientation (Chen et al., 2017). To take advantages of both small and large seeds, a multi-layer seeding was developed with seed powders of different sizes. During the synthesis, the small seeds on the top accelerated the nucleation kinetics and narrow the intercrystalline space. Besides, the gaps of the bottom layer consisting of large seeds were filled by the smaller seeds growing toward the support (Mirfendereski and Mazaheri, 2021).

Apart from seeding, the formation of zeolite membranes is influenced by the pH value. For example, when a low concentration of OH\(^-\) was fed in the mother liquor, the densification and complexation of silicate species were poor; however, a high pH value might slow down the Si-O-Si bond hydrolysis and crystal growth, and even cause the zeolite dissolution and silicate conversion, thus generating defects in the membrane layer (Hazrati et al., 2018; Hayakawa and Himeno, 2020; Pourazar et al., 2020). Therefore, a medium amount of OH\(^-\) was favored due to the accelerated nucleation kinetics and small crystal size (Wang et al., 2019b; Araki et al., 2021). The orientation is also affected by the pH value. In the synthesis of DDR zeolite membrane, a high pH value of the mother liquor led to a crystal growth toward various directions while a neutral pH could maintain the orientation at the beginning of the preparation (Nguyen et al., 2021). Besides the mother liquor, a careful addition of acids during the membrane post-treatment enables a better crystallization by removing the amorphous zeolite crystals without destroying the morphology. However, both the zeolite and silica crystals can be possibly dissolved under a strong acid treatment, deteriorating the membrane quality and performance (Zhu et al., 2019). Based on the above discussion, a medium alkaline condition (pH = 11–12) is mostly preferred for the synthesis of high-quality zeolite membranes (Hazrati et al., 2018; Hayakawa and Himeno, 2020). In certain scenarios, however, nearly neutral (pH = 7–7.5) or strong basic (pH = 14) environment enables the formation of zeolite membrane layers, such as Si-CHA and Si-DDR (Araki et al., 2021; Nguyen et al., 2021).

Owing to the polarity difference, the ratio of Si/Al exerts a profound impact on the hydrophobicity of the membrane surface (Lee et al., 2019; Liang et al., 2018). With a high content of Al, the polar surface benefits the adsorption of polar molecules, that is, CO\(_2\) in dry conditions and H\(_2\)O in humid environments (Yu et al., 2019a; Zhou et al., 2020a, 2020b). However, a large amount of Al may lead to poor crystal intergrowth and non-zeolitic pathway, thus lowering the membrane selectivity (Noack et al., 2006). To strike a balance, the optimal Si/Al window is suggested between 47 and 410 depending on the zeolite structure (e.g., CHA, SSZ-13, MFI, ZSM-5) according to the above research explorations. In addition to the Si/Al ratio, the gel concentration (SiO\(_2\)/H\(_2\)O ratio) determines the nucleation process, morphology, and structure of the zeolite membranes. A high gel concentration facilitates the nucleation and forms a thin layer; but the non-homogeneity of concentrated gel could lower the quality of the membrane (Zhang et al., 2020; Carreon et al., 2008; Van Heyden et al., 2008). Furthermore, the gel concentration relates strongly to the processing time. During the CHA zeolite membrane synthesis, a slow injection (e.g., over 24 h) was needed for the diluted gel to ensure the selectivity and durability of the membrane; in comparison, for the concentrated gel, a bit higher temperature (e.g., 373 K) was used to quicken the injection within 12 h without nano-scopic defects (Yang et al., 2019a).

Besides the chemical ratio in the mother liquor, the synthesis time strongly influences the crystallization process of zeolites. A characteristic growth mechanism of the membrane includes two steps, which are nucleation initiated by the seeds/small crystals, and a confined intergrowth of the crystals to produce a membrane layer (Wang et al., 2020a, 2020b). In this scenario, a short duration might generate defects, gaps, and particles with non-uniform morphologies since the dissolution, crystallization and intergrowth are not sufficient (Jang et al., 2018; Zhang et al., 2018). On the contrary, an overgrowth of the zeolite crystals under an excessively long duration can diversify the particle size and thicken the membrane layer (Liu et al., 2018a, 2018b, 2019, 2019). Even worse, a stable phase instead of the zeolite structure is formed under a prolonged time because the crystals are redissolved in alkaline solutions (Chen et al., 2017).

Temperature is another key factor to determine the zeolite membrane quality and physicochemical property, such as thickness, structure, size, and purity (Mirfendereski, 2019; Xu et al., 2017). A low temperature enables slow crystallization compared with nucleation, leading to a thin layer with few defects and small size (Qiu et al., 2020). On the other hand, a high temperature tends to produce a large crystal size owing to faster crystallization than nucleation. The large crystals strengthen the zeolite-support interaction and
facilitate molecular diffusion, but the poor selectivity might be a concern for separation and reaction (Mirmendereski, 2019; Hazrati et al., 2018). To strike a balance, two-step synthesis is a promising alternative to the one-pot method. In detail, a low temperature at the first step benefits the fast nucleation and allows the nuclei to move to the voids of the seed layer, which continue to grow in all directions to fill the gaps in the following step at higher temperatures. In comparison, the one-step heating method accelerates the crystal growth, producing a thicker and more defective membrane layer (Mirmendereski and Lin, 2020).

**Synthesis strategies**

To realize a good balance between nucleation and crystallization, organic structure-directing agents (OSDAs) are widely adopted in zeolite membrane synthesis. For example, compared with N,N,N-trimethyl-1-adamantammonium hydroxide (TMAdaOH), tetraethyl ammonium hydroxide (TEAOH) with a better solubility of silica and smaller molecular size enjoyed accelerated nucleation kinetics and lower removal temperature. As a mineralizing agent and phase controller, TEAOH enabled a small particle size and a thin zeolite layer with high surface area and homogeneity (Xu et al., 2020; Daeyaert and Deem, 2020; Araki et al., 2020). To further improve the continuity and achieve a defect-free membrane, uniform seed distribution and growth are needed. However, the deposition of zeolite precursor into the pores of support may produce defects within the membrane (invasion). To solve this problem, 1H,1H,2H,2H-perfluorodecyltrihydroxilane and poly(dimethylamine-co-epichlorohydrin-co-ethylenediamine) (ATC-4150) were added as the hydrophobization agent and cationic polymer, respectively. Via the electrostatic force, negatively charged seed crystals were easily adsorbed onto the cationic polymer; meanwhile, since the hydrophilic surface was covered by the hydrophobization agent and turned to be hydrophobic, the precursor invasion was greatly inhibited and a homogeneous seed distribution was approached (Yu et al., 2019b).

Despite the favorable effects of OSDAs on the zeolite crystal growth, the membrane quality might be adversely affected during the elimination of OSDAs. If they are not completely removed, the diffusion of molecules can be retarded since the pores are blocked by the deposited OSDAs (Yang et al., 2019b). To ensure full elimination, a high temperature is favored but may also cause thermal stress and crack generation since the zeolite and support materials possess different thermal expansion coefficients (Dong et al., 2000). Therefore, several mild heating methods have been proven successful to overcome the above challenges. For example, the application of ozone effectively lowers the temperature due to strong oxidability. Compared with the serious strains and cracks formed when 1-adamantanamine (ADA) was removed from air during the DDR membrane synthesis, the activation temperature was almost decreased by half with ozone (Wang et al., 2017; Hayakawa and Himeno, 2021). The resulting membrane was much less defective despite the prolonged operation (Wang et al., 2019c, 2019d). To further lower the temperature, ultraviolet (UV) irradiation is proven effective in eliminating the OSDAs at nearly ambient conditions. Under the UV activation, the OSDAs were excited to produce ions, molecules, and radicals, which reacted with the oxygen atoms and ozone molecules derived from the O2 dissociation. As a result, the OSDAs were converted to gaseous products such as CO2, H2O, and N2, which easily escaped from the zeolite pores, thus obtaining a defect-free surface (Yang et al., 2019b).

In comparison to the mild removal of OSDAs, substitution by inorganic SDAs enables a completely heating-free process for SDA elimination, thus avoiding the thermal stress and crack formation, and saving the operation cost and energy consumption (Kim et al., 2013a, 2013b; Rangnekar et al., 2015). The promotional effect of inorganic SDAs has been proven when KOH or NaOH was used in the synthesis of SSZ-13 membrane; however, lattice expansion, strong electrostatic repulsion, and micropore blocking initiated by the high content of alkali ions could reduce the surface area, and effective porosity (Jang et al., 2018; Zhou et al., 2013). To address these issues, the incorporation of fluoride ions with alkali ions realized a synergy, promoting the alkaline hydrolysis of SiF6^2- species and intergrowth of CHA zeolite crystals, thus improving both the purity and continuity of the membrane (Liu et al., 2019).

In addition to OSDA-free synthesis, a gel-free process is a promising alternative to the conventional method where the precursor gels have to be aged. Benefitting from the gel-free secondary growth, the membrane synthesis turns out to be safer, more environmentally friendly, less expensive, and simpler in operation (Le et al., 2020; Tang et al., 2021a; Nguyen et al., 2021). For instance, with kaolin as the substrate, the compositional elements were provided from the support, and the SAPO-34 and AlPO-18 zeolite membranes were formed in situ. The thinner, more oriented, and more continuous layer structure produced in the gel-free strategy was attributed to the inhibited partial dissolution of seed crystals (Le et al., 2020).
Other than the OSDA-assisted, OSDA-free, and gel-free strategies, some techniques can be integrated into the membrane synthesis to reduce the thickness. For example, recirculated flow system increased the homogeneity of the precursor solution and the resulting SAPO-34 zeolite layer was 25% thinner than that prepared in the conventional autoclave. Notably, the flow rate needed to be optimized to ensure fast crystallization and avoid turbulence (Topuz et al., 2017). Another way to obtain a thin zeolite layer is to shorten the heating time. Microwave heating or oil bath followed by rapid thermal processing (RTP) have been successfully applied to reduce the thermal lag and accelerate the crystallization kinetics (Zhang et al., 2016; Wang et al., 2019c, 2019d; Bai et al., 2017). Moreover, in the RTP where the membrane gel was heated in an liner-free autoclave, the thermal stress was alleviated with the bond formation of crystals (Chang et al., 2018; Hayakawa and Himeno, 2021; Bai et al., 2017). In another scenario where hot-dipping method was applied to realize a quick synthesis, the autoclave was preheated for 60 min followed by being turned upside down to allow a contact between the seeded tubes and mother liquor. By doing so, a small crystal size and a thin membrane layer were approached (Figure 2) (Tang et al., 2021b). As mentioned above, both a homogeneous precursor solution and a rapid heating process contribute to a thin zeolite layer; however, defects or boundary gaps can be formed when the thickness is reduced up to a certain extent. Assisted by vacuum-assisted deposition (VAD) technique, the zeolite surface could be coated with a layer of organosilica to patch the gaps. With an optimized number of deposition cycles, both the over-loading of fillers and insufficient filling were inhibited (Mu et al., 2019). In the above synthesis, hydrothermal treatment is a necessary step; however, it is criticized for the generation of chemical hazards and energy consumption (Ayele et al., 2016). By utilizing the high-power ultrasound, energy could be supplied from acoustic cavitation so as to activate the chemical bonds, producing free radicals and accelerating the crystallization (Bang and Suslick, 2010). It was noteworthy that regarding this strategy, the condensation of molecules might negate the formation of the zeolite membrane (Sen et al., 2018).

**STRUCTURE AND SURFACE PROPERTIES OF ZEOLITE MEMBRANES**

The diffusion of gaseous molecules is considerably affected by several properties, such as the thickness, defects, orientations, and hydrophobicity of zeolite membranes, which relates strongly with the gas...
separation from upstream mixtures and the conversion efficiency of the downstream reactions. In the following sections, these surface and structure properties will be illustrated with examples to demonstrate the determining factors of the properties and the impacts of these properties on the membrane performances.

**Thickness**

The morphology of seeds exerts an influence on the thickness and quality of the membrane. For example, a thin zeolite layer is formed benefiting from the strong gel attachment and crystal imperfection during the epitaxial growth of cubic seeds with a hierarchically porous structure. In comparison, a thick layer is produced from the intergrowth of ellipsoid solid seeds (Liu et al., 2018a, 2018b; De Yoreo et al., 2015; Meng et al., 2014; Gomez et al., 2015). In another case where rectangular thin plate seeds are adopted, the poor intergrowth of crystals leads to poor performance in the gas-tight test despite the thin membrane structure (Zhang et al., 2020). Besides the morphology, the seed concentration plays a critical role in the thickness of the membrane. At a low concentration, the membrane is thin but with gaps and cracks because of the restricted crystal growth; at a high concentration, a thicker layer will decrease the effective tortuosity and increase the transport pathway (Wang et al., 2019c, 2019d). To achieve a homogeneous and dense membrane, sufficient nucleation and complete coverage of the porous support are required, which is enabled by an optimal amount of seeds (Kida et al., 2018). Moreover, a thin membrane layer can be developed by facilitating the nucleation/crystallization and minimizing the thermal lag with a suitable treatment method, such as microwave heating, rapid thermal processing, and mild treatment (Qiu et al., 2020; Wang et al., 2019c, 2019d; Tang et al., 2019). The potential problems of these methods include the larger crystals formed during the prolonged synthesis and the structure collapse caused by the overheating (Qiu et al., 2020).

**Defects**

Defects usually refer to the intercrystalline pores with a larger size than the intracrystalline pores (i.e., zeolite channels), which originate from either the linear expansion difference of support and zeolite materials or the insufficient zeolite crystal growth (Al-Akwaa et al., 2021; Vaezi et al., 2018). The gas diffusion is promoted with more defects or an enlarged defect at the cost of selective permeation. To tune the defect concentration and size so as to balance the permeability and selectivity, linking agents are helpful by strengthening the zeolite-support interactions with hydrogen bonding or electrostatic force (Zhu et al., 2020; Mubashir et al., 2020). Also, additive molecules can heal the defects and improve the effective porosity of zeolite membranes by filing the intercrystalline space (van den Bergh et al., 2010; Aydani et al., 2021). Compared with the additives, the impacts of thermal treatment are complicated. On one hand, a rapid heating process strengthens the chemical bonding between zeolite crystals, resulting in fewer defects (Choi et al., 2009; Chang et al., 2018). On the other hand, template removal under high temperatures may produce cracks (Wang et al., 2017; Chang et al., 2018; Jeong et al., 2021; Karakiliç et al., 2019; Hayakawa and Himeno, 2021). Apart from the processing conditions, the defect formation is determined by the support pore size. In particular, defects are prone to forming in the presence of large support pores because of incomplete coverage. While for the support with a small pore size, the pore-filling is facilitated and fewer cracks are generated (Tawalbeh et al., 2013; Li et al., 2008; Deng et al., 2010).

**Orientations**

The crystal channel alignment determines the gas transport pathway, diffusion distance, and entrance to the pore (Rangnekar et al., 2015). For example, the diffusion coefficient was much higher in the all-silica MFI zeolite with b-orientation and [010] channels than those perpendicular channels to [010] ones (Caro et al., 1993). In another scenario where large amounts of small seeds were present on the top of the ZSM-5 (MFI) membrane, crystallization in c-orientation was exhibited, which favored the out-of-plane growth rather than in-plane direction, realizing a highly selective CO₂ permeation (Mirfendereski and Mohammadi, 2011; Banihashemi et al., 2018; Mirfendereski and Mazaheri, 2021). Similarly, CO₂ diffusion was promoted in the CHA zeolite membrane with an out-of-plane orientation due to the short transport pathway (Lee et al., 2019). However, in the DDR zeolite membrane formed from the epitaxial growth of MCM-22 seeds, a low CO₂ molar flux was demonstrated with an out-of-plane orientation (Jang et al., 2020). To take advantage of both the in-plane and out-of-plane growth, the AIPO-18 zeolite membrane with mixed orientations was prepared with hydrothermal treatment. Featured with the sandwich-like hierarchical microstructure formed from the alternatively in-plane, out-of-plane, and in-plane crystal growth, CO₂ diffusion and selectivity were both enhanced (Wang et al., 2019a).
Hydrophobicity
In the CO₂-involved reactions (e.g., CO₂ hydrogenation and DRM), the competitive adsorption of H₂O is unavoidable in most cases. Therefore, the surface hydrophobicity needs to be well-adjusted to promote the conversion of CO₂ (Rehman et al., 2019). In principle, the zeolite membrane with a high Si/Al ratio exhibits a hydrophobic surface (e.g., SSZ-13 and DDR), where CO₂ adsorption and diffusion are facilitated. On the contrary, a high concentration of Al renders the zeolite membrane more hydrophilic, thus promoting water adsorption and permeation (Lee et al., 2019; Jeong et al., 2019; Kosinov et al., 2014). To enhance CO₂ adsorption, capping agents can be added to cover the hydroxyl groups. Integration with another hydrophobic zeolite is also an option (Rehman et al., 2019; Yu et al., 2019b; Wang et al., 2021). Moreover, complete elimination of OSDAs benefits CO₂ transport by reducing the hydrophilic residues within the membrane structure (Jeong et al., 2021). However, if the target is water removal such as in the methanol production from CO₂ and H₂, a hydrophilic surface might be preferable to the hydrophobic one (Raso et al., 2021).

APPLICATIONS OF ZEOLITE MEMBRANES IN CO₂ CONVERSION REACTIONS
Owing to the satisfactory thermal and chemical stability, inorganic membranes are widely applied in high-temperature reactions. In particular, the integration of zeolite membranes will remove the product immediately so as to drive the forward reaction to overcome the thermodynamic limitation, enhancing the CO₂ conversion efficiency and product yield. In the following sections, two representative reactions (CO₂ hydrogenation and DRM) will be covered and the impacts of various types of zeolite membranes on the catalytic performances will be discussed.

CO₂ hydrogenation to methanol
In CO₂ hydrogenation to methanol, the conversion is limited by the thermodynamic equilibrium and side reaction (Equations 1 and 2) (Yue et al., 2021). Also, to obtain a relatively acceptable methanol yield in industry, a high pressure of 5–10 MPa is usually required. By removing the products from the reactor, low pressure is enabled for the operation and a low flow rate is provided in the re-circulation loop (Gorbe et al., 2018). Therefore, in order to increase the CO₂ conversion and methanol yield and to save the energy input and operation cost, zeolite membranes can be utilized by promoting product elimination during the reaction (Gallucci and Basile, 2007; Iwakiri et al., 2022). In Tavolaro’s study, the LTA zeolite (zeolite A) membrane loaded with the Cu/ZnO/Al₂O₃ catalyst was directly used as the reactor for CO₂ hydrogenation to methanol (Figure 3A). As shown in Figure 3B, the crystalline layer at the inner surface of the tubular membrane exhibited a uniform morphology. Moreover, in the enlarged micrograph (Figure 3C), large amounts

![Image](image_url)
of cubic zeolite crystals were interconnected with each other, suggesting homogeneous nucleation. In the reaction between 210 and 220°C, the CO₂ conversion values of the zeolite membrane reactor were around twice those of the TR module, indicating a significant enhancement of the catalytic performance in CO₂ hydrogenation reaction with the help of the LTA zeolite membrane (Table 1) (Tavolaro and Tavolaro, 2007).

\[
\text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \Delta H_{298K} = -49.5 \text{kJ mol}^{-1} \tag{Equation 1}
\]

\[
\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H_{298K} = +41.2 \text{kJ mol}^{-1} \tag{Equation 2}
\]

To further investigate the effect of zeolite A membrane, Raso et al. (2021) compared five zeolite membranes, that is, zeolite T, mordenite, zeolite A, chabazite, and Ti-chabazite in terms of the separation factor and reaction performance. Results showed that both H₂O/CO₂ and H₂O/H₂ separation ratios followed the order: zeolite A > zeolite T > mordenite. Also, the H₂O/H₂ ratio of zeolite A was higher than those of chabazite and Ti-chabazite. The better permselectivity of H₂O was attributed to the higher Al content of zeolite A, rendering it more hydrophilic than counterparts. When the zeolite membrane reactor (ZMR) was coupled with the conventional packed bed reactor (TR) loaded with the CuO/ZnO/Al₂O₃ catalyst, TR + ZMR exhibited a higher conversion and yield in all reactions temperatures in this work, suggesting the positive impact of the ZMR on shifting the reaction equilibrium by selectively permeating H₂O (Figures 4A and 4B). Also, between 220 and 240°C, the yield of methanol was beyond the equilibrium value. As for the much higher CO₂ conversion than the methanol yield, a reasonable explanation was the reverse water-gas shift reaction (RWGS) (Equation 2), which was more favorable than hydrogenation when the H₂O was removed from the system. Meanwhile, the opposite trend of the CO₂ conversion and methanol yield could be explained by the fact that both the targeted and side products were formed with an enhanced CO₂ conversion of 15% (Table 1); therefore, the selectivity might be reduced accordingly.

The conventional Cu/ZnO/Al₂O₃ catalyst suffers from the metal agglomeration and reduced surface area induced by the steam product, resulting in a deactivation during the reaction. Also, the activity is worsened due to the competitive RWGS reaction (Liang et al., 2019; Prasnikar et al., 2019). To prevent metal sintering and enhance the catalytic performance, a highly active and robust catalyst is expected to be developed. The addition of ZrO₂ can strengthen the interaction between Cu and metal oxides, thus improving the Cu dispersion and anti-sintering property (Gao et al., 2013a, 2013b, 2013b; Arena et al., 2009). By coupling with the LTA zeolite membrane (catalytic membrane reactor, CMR), a high CO₂ conversion of 36.1% and methanol selectivity of 100% were achieved at 260°C and 3.0 MPa ascribed to the synergy of catalyst and membrane (Figure 3A). In detail, compared with the Cu/ZrO₂ and Cu/ZnO catalysts, Cu/ZnO/ZrO₂ enjoyed improved adsorption of CO₂ and hydrogenation of carbonate species to reactive intermediates (e.g., methoxy and formate) (Wang et al., 2019c, 2019d). On the other hand, the hydrophilic LTA membrane was highly active for adsorbing the polar molecules (e.g., CH₃OH and H₂O) due to the existence of Na⁺ while those non-polar components (e.g., H₂, CO₂, N₂) were weakly adsorbed in the membrane (Figure 5A).

Furthermore, owing to the stronger hydrophilicity and less bulky size than CH₃OH, H₂O molecules were preferred to be permeated through the membrane, thus overcoming the thermodynamic limitation and preventing the side product formation and catalyst deactivation (Figure 5B). A comparison with other membrane reactors was conducted to further demonstrate the advantages of CMR (Figure 5C). The results showed that both the CO₂ conversion and CH₃OH selectivity of CMR were higher than those of the counterparts, which was attributed to the synergistic effects of the high active/stable catalyst and highly selective membrane. Over a 90-h stability test, the CO₂ conversion and CH₃OH selectivity were kept constant at 36 and 100% respectively, suggesting a greatly inhibited Cu oxidation and ZnO sintering at the reaction conditions (Figure 5D and Table 1) (Yue et al., 2021).

Apart from the modification of catalyst, the catalytic conversion of CO₂ and yield of CH₃OH can be increased with the increase of H₂O permeance and H₂O/CH₃OH permselectivity of the membrane, which is closely related to the surface hydrophobicity and hydrophilicity. Particularly, when the Si/Al ratio in the LTA membrane was enhanced from 1 to 1.5, the compensation Na⁺ ions became fewer, thus promoting the H₂O diffusion through the membrane. Meanwhile, the Si-rich structure turned out to be less hydrophilic, which reduced the permeation of CH₃OH to a much larger extent than H₂O due to the lower hydrophilicity of CH₃OH (Figure 6A). Therefore, a high H₂O permeance of 1.5×10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ and a high selectivity of H₂O/CH₃OH of 2000 was achieved at 473 K (Seshimo et al., 2021). Furthermore, a much higher CO₂ conversion (60%) was obtained in the Si-rich LTA membrane loaded with the Cu/ZnO catalyst compared with that of only 20% obtained in the packed bed reactor without the membrane. Notably, the morphology
| Membrane | Catalyst | Membrane synthesis | Separation factor | Reaction type | Reaction temperature (°C) | CO₂ conversion (%) | Product yield or selectivity (%) | Ref |
|-----------|----------|-------------------|------------------|--------------|--------------------------|-------------------|-------------------------------|-----|
| Zeolite A | Cu/ZnO/Al₂O₃ | Hydrothermal | H₂/N₂ = 3.35 | CO₂ hydrogenation to methanol | 215 | 14 | N.A. | Tavolaro and Tavolaro (2007) |
| Zeolite A | CuO/ZnO/Al₂O₃ | Secondary growth method | H₂O/CO₂ = 750; H₂O/H₂ = 270 | CO₂ hydrogenation to methanol | 240 | 15 | 0.5 | Raso et al. (2021) |
| Zeolite A | Cu-ZnO/Al₂O₃-ZrO₂ | Hydrothermal | H₂O/CH₃OH = 257; H₂O/CO₂ = 51.6; H₂O/H₂ = 0.33 | CO₂ hydrogenation to methanol | 260 | 36 | 100 | Yue et al. (2021) |
| Zeolite A | Cu/ZnO | Hydrothermal | H₂O/CH₃OH = 2000 | CO₂ hydrogenation to methanol | 210 | 23.9 | 60.2 | Seshimo et al. (2021) |
| Zeolite membrane (Modeling) | Cu/ZnO/Al₂O₃ | N.A. | H₂O/CH₃OH = 2500 | CO₂ hydrogenation to methanol | 230 | 8.3 | 51 | Gallucci and Basile (2007) |
| sodalite (SOD) (Modeling) | Cu/ZnO/Al₂O₃ | N.A. | H₂O/CH₃OH = 134.6 | CO₂ hydrogenation to methanol | 270 | 24 | 18.2 | Iwakiri et al. (2022) |
| ZSMS/MFI | Cu-ZnO-Al₂O₃/HZSM-5 | N.A. | H₂O/H₂ = 18 | CO₂ hydrogenation to DME | 227 | 0.69 | 0.99 | De Falco et al. (2017) |
| Zeolite membrane (Modeling) | Cu-ZnO-Al₂O₃/HZSM-5 | N.A. | H₂O/CH₃OH = 10; H₂O/CO₂&CO = 30; H₂O/H₂ = 50 | CO₂ hydrogenation to DME | 200 | 36 | 43 | Poto et al. (2021) |
| LTA | CuO-ZnO-ZrO₂/SAPO-11 | Hydrothermal | C₂H₅OH/H₂O = 2905; CH₃OH = 1011 | CO₂ hydrogenation to DME | 275 | 20 | 12 | Rodriguez-Vega et al. (2021) |
| sodalite (SOD) | Cu-ZnO/Al₂O₃ | N.A. | H₂O/H₂ = 4.6; H₂O/CO₂ = 22.6 | CO₂ hydrogenation to DME | 250 | 12.4 | 33.2 | Koybasi and Avci, 2022 |
| NaY | NiO-La₂O₃/γ-Al₂O₃ | in situ crystallization | H₂/CH₄ = 1.9; CO/CO₂ = 1.6 | DRM | 700 | 72.7 | H₂/CO = 0.87 | Liu and Au (2001) |
| NaY | NiO/γ-La₂O₃ | Dip-coating | H₂/CH₄ = 4.2 | DRM | 700 | 82.44 | H₂/CO = 0.78 | Liu et al. (2002) |
| Pd/NaY | Rh/La₂O₃ | Dip-coating and hydrothermal | H₂/CH₄ = 215 | DRM | 450 | 98.5 | H₂ purity = 99.5% | Bosko et al. (2010) |

Remarks: N.A., not available; DME, dimethyl ether.
and particle size of the Si-rich LTA membrane were similar to the pristine one, suggesting an exclusive impact of the Si content on the separation and reaction performances (Figures 6B and 6C). In another scenario where hydrophilic membrane B and organophilic membrane A were compared, membrane B exhibited a higher CO₂ conversion (23.9 vs. 22.7%) while membrane A presented a higher methanol selectivity (60.2 vs. 54.2%) at 210°C and 10 bar (Table 1). As for the activity, more water permeation via the hydrophilic membrane B promoted the shift of forward reaction, thus increasing the CO₂ conversion. In comparison, both the CO₂ hydrogenation and RWGS reaction were facilitated with the removal of H₂O; moreover, RWGS was more sensitive to the water concentration gradient. Therefore, more CO rather than methanol was produced and the CH₃OH selectivity was correspondingly reduced for the hydrophilic membrane B (Barbieri et al., 2002).

**CO₂ hydrogenation to dimethyl ether**

DME is widely used as a reagent for the production of light olefins, methyl acetate, and dimethyl sulfate. Also, it can be applied as an aerosol propellant in the chemical industry (Kang et al., 2008). Moreover, DME is a promising alternative fuel to be utilized in compression-ignition engines (Arcoumanis et al., 2008). One route for DME production is via the dehydration of methanol synthesized from the hydrogenation of CO and CO₂, which is the so-called two-step method. In comparison, the direct method (i.e., one-step mode) possesses several merits, such as compactness, low cost, and high productivity; therefore, one-step strategy is preferred in the industry (Arcoumanis et al., 2008). During the process, the simultaneous formation of methanol and DME from CO₂ hydrogenation in a single reactor is catalyzed by either the mixture of Cu/ZnO/Al₂O₃ (for methanol synthesis, Equation 1) and Cu-ZnO-HZSM-5 (for methanol dehydration, Equation 3) or the bifunctional catalyst Cu-ZnO-Al₂O₃/HZSM-5 (De Falco et al., 2017). Although strong adsorption of CO₂ was observed at the catalyst surface, the existence of CO₂ might drive the competitive RWGS reaction to consume the hydrogen gas, thus negating methanol production and dehydration. To simultaneously approach the elimination of CO₂, alleviation of the greenhouse effect, and production of DME in a one-pot reaction, integration with H₂O-selective membranes is a promising solution, especially for the DME synthesis from CO₂-rich raw feeds (Centi et al., 2013; De Falco et al., 2011; Iulianelli et al., 2010). Among various types of membrane materials, zeolites possess an ordered crystal structure and homogenous pore size distribution, benefiting gas diffusion through the membrane. More importantly, the high H₂O permselectivity and strong chemical/thermal stability render zeolite membranes a relatively ideal candidate for DME synthesis from CO₂ and H₂ which usually occurs at 200–300°C and 30–70 bar (Table 1) (De Falco et al., 2017; Rodriguez-Vega et al., 2021; Koybasi and Avci, 2022). The schematic diagram of the catalytic membrane reactor used for DME production is shown in Figure 7. In the hollow tubular reactor, the reaction zone locates at the outside layer (shell) while the H₂O produced was permeated into the core part, where the H₂O was removed by sweeping. To satisfy the CO₂ valorization framework and convert CO₂ into value-added products as possible, pure CO₂ stream can be fed into the permeation zone as a sweep gas to carry the resulting H₂ and H₂O. After condensation, the remaining CO₂ and H₂ streams are added to the reaction zone to continue the hydrogenation to the DME process (De Falco et al., 2017).

\[
2\text{CH}_3\text{OH} \leftrightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \quad \Delta H_{298K} = -23 \text{ kJ} \cdot \text{mol}^{-1} \quad \text{(Equation 3)}
\]
The most commonly studied zeolite membranes are Mordenite (MOR) with a large pore dimension of 0.65 \times 0.70 \text{ nm}, ZSM-5/MFI membranes with a medium pore dimension of 0.51 \times 0.55 \text{ nm}, and LTA with a pore width of 0.398 \text{ nm} (Bernal et al., 2000; Ateka et al., 2021). For example, CuO-ZnO-ZrO2@SAPO-11 core-shell structured catalyst has been proven highly active for DME direct synthesis from CO2 and H2 (Sanchez-Contador et al., 2018). When the LTA membrane coupled with the CuO-ZnO-ZrO2/SAPO-11 catalyst was applied in the DME synthesis from CO2 hydrogenation, 17% CO2 conversion and 5% DME yield were achieved at 325°C and 40 bar, which were twice those of the packed bed reactor without the membrane (Ateka et al., 2021). In another case where a 1D phenomenological reactor model was applied to analyze the influences of membrane reactor on the CO2 conversion and DME yield, the results predicted that compared with the conventional packed bed reactor, if 96% of the water produced from the reaction was eliminated by the membrane, the CO2 conversion and DME yield were improved by 36 and 43% respectively at 200°C and 40 bar (Figure 8A) (Poto et al., 2021). Moreover, since the reaction rate reached the maximum value at the initial stage of the reaction, both the water concentration and heat approached the highest near the inlet of the reactor (Figure 8B). Therefore, a co-current circulation was necessary to exert the highest driving force in order to eliminate the heat and water effectively, which increased the DME yield from 44% to 64% (Poto et al., 2021). Furthermore, to elucidate the critical role of hydrophilic zeolite membrane in CO2 hydrogenation to DME, a series of separation ratios (H2O/H2, H2O/COx, and H2O/CH3OH) were investigated in terms of the water permeation effect on the operation and performance. First, when the H2O/H2 was low, H2 co-feeding (back permeation) would occur, favoring the DME yield and CO2 conversion (Diban et al., 2013b). However, co-feeding might not be desirable since a significant H2 reintegration was required in the sweep gas. Also, a high H2O permselectivity enabled a direct re-circulation and avoided the complicated post-processing units (Poto et al., 2021). Second, a high H2O/COx ratio limited the loss and co-feeding of COx, which simplified the re-circulation because the COx composition in the sweep gas was not necessarily tuned. Meanwhile, the restricted CO2 diffusion minimized the reaction degree of RWGS, thus leading to a high DME selectivity (Poto et al., 2021). Third, although the CH3OH permeation drove the equilibrium of CO2 hydrogenation, it was not favorable for DME production because methanol dehydration was the key step to form DME. Therefore, a high H2O/CH3OH was preferred so as to maintain the CH3OH concentration in the reaction zone, benefiting the further conversion to DME (Table 1).
Based on the above discussions, a relatively high H$_2$O permselectivity not only increased the CO$_2$ conversion but also enhanced the DME yield, indicating the crucial influences of the H$_2$O-selective zeolite membrane.

To further enhance the synergy between the catalyst and membrane, an HZSM-5 membrane packed with CuO-ZnO-Al$_2$O$_3$ catalyst was developed for DME synthesis from CO$_2$ and H$_2$ (Liu et al., 2015). Owing to the homogeneous pore distribution, uniform thickness and fixed position of the HZSM-5 membrane, the methanol intermediate formed at the surface of the catalyst would diffuse smoothly out of the catalyst bed, thus inhibiting the formation of side products such as alkanes and alkenes (Yang et al., 2010). Moreover, the catalyst deactivation (e.g., sintering and carbon deposition) was effectively alleviated due to the easy desorption and diffusion of products, and the isolation of nanoparticles by the hollow space and pore structures of HZSM-5, thus prolonging the catalytic stability for DME production (Liu et al., 2011).

Dry reforming of methane

Besides the CO$_2$ hydrogenations, the DRM reaction converts two greenhouse gases (CO$_2$ and CH$_4$) into syngas (CO and H$_2$), which simultaneously alleviates the environmental issues and brings industrial economic benefits (Ni et al., 2012, 2013, 2016, 2013, 2016; Gao et al., 2015a, 2015b, 2016, 2017, 2020a, 2015b, 2016, 2017, 2020a). Based on Le Chatelier-Braun’s law, the removal of the products will shift the forward reaction to overcome the thermodynamic limitation, considerably increasing both the conversion and selectivity. Zeolite membranes (e.g., ZSM-5) have been proven highly permselective toward hydrogen gas. Therefore, the integration of zeolite membranes with the active catalysts exhibits potential in enhancing the DRM reaction performances. For example, when NiO-La$_2$O$_3$/γ-Al$_2$O$_3$ catalyst (responsible for CO$_2$ adsorption and CH$_4$ activation) was loaded on the NaY zeolite membrane, the CO$_2$ and CH$_4$ conversions were increased from 66.7% to 72.7% and from 49.5% to 70.96% respectively compared with the fixed bed reactor, which could be attributed to the selective H$_2$ permeation through the membrane reactor and the promoted CH$_4$ decomposition over the catalyst as a consequence (Figure 9A, Table 1). Also, the activities were maintained for 6 h, suggesting stabilized conversions and anti-deactivation properties. It should be noted that according to the single gas permeation test, the separation factor of H$_2$/CH$_4$ reached as high as 9.2, outperforming the 2.8 determined by the Knudsen diffusion mechanism, suggesting a defect-free membrane layer (Figure 9B). However, the H$_2$/CH$_4$ ratio was lower than the Knudsen diffusion value in the binary gas permeation test, which could be explained by the hindrance effect of the strongly adsorbed CH$_4$ molecules on the diffusion of hydrogen gas (Liu and Au, 2001).

In another study where the same catalytic membrane reactor was applied in the DRM reaction, the promotional effect of the NaA membrane on the coke resistance was elucidated. In particular, over a 10-h reaction
test at 700°C, the coke formation in the membrane reactor was 4-5% while that in the conventional reactor was 7–11%, which led to higher catalytic stability of the membrane reactor (Table 1). The less coke deposition could be ascribed to the extra CO2 conversion driven by the immediate removal of CO and H2. Meanwhile, a higher Ni dispersion was obtained on the NaA zeolite layer, resulting in less possibility of carbon deposition. Moreover, the deposited carbon species were able to be accommodated by the membrane channels while the diffusion of active sites into the pores was restricted by the homogenous microporous structure of the membrane, which segregated the cokes from the catalyst rather than covering the catalyst surface (Liu et al., 2002).

In addition to the above beneficial effects on the permeation and reaction, the NaY membrane could act as a stabilizing layer to anchor the Pd metals. In detail, the oxidized stainless steel support was modified with the NaY membrane derived from the cubic crystals (Bosko et al., 2009). Owing to the synergistic effects of both Pd layer and NaY membrane on the stainless steel support, the H2 permselectivity maintained stable at 450°C for 250 h (Table 1). Also, the enhancement of CH4 conversion was over 80% at 450°C (Bosko et al., 2010).

**IMPACTS OF OPERATION CONDITIONS**

In the CO2 hydrogenations and DRM reaction, the permeance, permselectivity, and catalytic performances are not only related to the intrinsic properties of the membrane and catalyst, but also determined by the process parameters, such as the reaction temperature, total pressure, pressure drop, sweeping rate, feed ratio, feed rate, gas hourly space velocity (GHSV) and re-circulation rate. In the next sections, the impacts of operation conditions will be discussed in a comprehensive and critical way.

**Temperature**

Considering the exothermic CO2 hydrogenation and endothermic RWGS reaction, a low reaction temperature is thermodynamically favored for a high methanol/DME yield and CO2 conversion (Seshimo et al., 2021; Barbieri et al., 2002; De Falco et al., 2017; Liu et al., 2015). For example, when zeolite A membrane reactor was applied for CO2 hydrogenation at a pressure of 5 bar and H2/CO2 of 3, the CO2 conversion presented a 3-fold increase while the methanol yield dropped by half when the temperature was increased from 200°C to 240°C (Raso et al., 2021). To overcome the thermodynamic limitation, in-situ water permeation through the membrane plays a critical role in driving the equilibrium to produce more methanol and convert more CO2, which also relies heavily on the operation temperature. Specifically, the permeation via the LTA zeolite (zeolite A) membrane behaved like a vapor at a temperature lower than 238°C while the methanol yield was higher than 238°C but like a gas when the temperature was higher than 238°C. The former permeation followed the capillary condensation mechanism while the latter one followed the Knudsen mechanism. For the later one, a non-selective permeation occurred, which resembled the conventional reactor without a membrane (Tavolaro and Tavolaro, 2007; Barbieri et al., 2002).

The water permeation is controlled by diffusivity and adsorbed molecule concentration. At the low-temperature region, a increase in temperature facilitates the diffusion of water vapor, resulting in a larger water flux. At the medium temperature zone, a temperature increase intensifies the desorption of molecules and...
reduces the adsorbed water concentration, thus lowering the molar flux. When the temperature goes to a high value, the water flux is enhanced again but mainly in the gas phase with very low selectivity, similar to the Knudsen mechanism (Arruebo et al., 2001). Taking methanol synthesis as an example, with the NaA zeolite membrane, the methanol selectivity dropped sharply from 73% to 46% with the temperature increasing from 240°C to 250°C, indicating that careful control of the temperature is necessary to strike a good balance between the activity, selectivity, and energy consumption (Tran et al., 2017).

From a kinetic view, a reaction temperature enhancement will increase the reaction rate, especially at a relatively low-temperature zone (Hu et al., 2018). When the temperature goes to a high value, despite the fast intrinsic reaction rate, a reduced catalytic activity might be seen. Except for the thermodynamic limitations (e.g., exothermic nature and side reaction), the catalyst deactivation is another concern. Particularly, a high temperature may destroy the active sites by intensifying the particle agglomeration and lowering the metal dispersion (Ren et al., 2015).

Different from CO2 hydrogenation which is exothermic, DRM reaction is strongly endothermic and a high temperature benefits both the reaction rate and thermodynamic equilibrium. By integrating the H2-selective membrane with the catalyst, the catalytic membrane reactor enjoys a higher performance than the conventional one. Notably, at a high temperature, the separation factor of H2/CH4 turns out to be lower because of the stronger adsorption of CH4 than H2 at elevated temperatures. The pore blockage by CH4 hinders the diffusion of H2 through the membrane, thus deteriorating productivity (Liu and Au, 2001).

**Pressure**

The influence of pressure drop at both the feed and permeation sides depends on the defects of the membrane (De Falco et al., 2017; Tran et al., 2017; Poto et al., 2021). When the total pressure is the same on both sides, the unwanted non-selective diffusion can be greatly alleviated regardless of the defects of the membrane. When the pressure at the feed zone is higher than that at the permeation zone, the water diffusion is promoted in a defect-free zeolite layer; but in the membrane with defects, a pressure difference may cause the non-selective permeation via the intercrystalline pores, negating the conversion efficiency and methanol yield (Gorbe et al., 2018). Besides the pressure drop, by keeping the total pressure the same at both sides of the membrane, an absolute enhancement of the total pressures would bring a benefit for the water permeation because the interaction between the catalyst and reactant is strengthened at a high pressure and the number of molecules decreases for the forward reaction of CO2 hydrogenation according to the Le Chatelier’s principle (Yue et al., 2021; Seshimo et al., 2021; De Falco et al., 2017). Meanwhile, the large water partial pressure discrepancy generated at a high total pressure also favors the water permeation and reaction performance (Gorbe et al., 2018). In certain conditions, however, the water permeation is not determined by the partial pressure difference but is driven by the concentration gradient of adsorbed water vapor on both sides. This could be explained by the higher temperature at the external surface (e.g., AT = 30°C) which is directly heated (Ryazantsev and Kurnoskina, 1976). In addition, the operation cost and equipment maintenance along with the high pressure should also be carefully considered to satisfy industrial methanol production (Yue et al., 2021).

![Figure 8](image-url) (A) CO2 conversion and DME yield profiles of membrane reactor against the thermodynamic equilibrium values of conventional reactor. (B) Temperature and water molar fraction profiles of membrane reactor performances. Reproduced with permission from (Poto et al., 2021). Copyright 2021, Elsevier.
An interesting phenomenon is to be discussed regarding the pressure effect on the membrane reactor performances for different reactions. In methanol synthesis, a high pressure promotes both CO2 conversion and methanol yield. This is consistent with the DME production at high pressures. However, the DME selectivity is reduced in this scenario because of the insensitivity of subsequent methanol dehydration to the pressure change compared with the production of methanol as an intermediate or the side reaction RWGS to produce CO (De Falco et al., 2017; Liu et al., 2015).

**Feed ratio**

According to the chemical equation of CO2 hydrogenation to methanol and DME (Equations 1 and 3), with a constant total flow rate, a high H2/CO2 ratio leads to a high conversion of CO2 because the equilibrium shifts to the right (De Falco et al., 2017; Tran et al., 2017; Ateka et al., 2021). Also, as the H2 owns a higher reaction order than CO2, the number of CO2 molecules reacting with the H2 becomes higher in percent. As shown in Figures 10A and 10A increase in the H2/CO2 ratio from 3 to 7 exhibited enhancement of CO2 conversion in both membrane reactor and traditional reactor. For the CH3OH selectivity, different from the traditional reactor where the selectivity is positively correlated with the H2/CO2 ratio, in the membrane reactor, the impacts of the H2/CO2 ratio were only observed at low temperatures. At a high temperature, the contribution of temperature would become dominant (capillary condensation turning to be Knudsen mechanism) rather than the feed ratio (Figure 10B) (Gallucci et al., 2004).

On the other hand, despite the benefits of a high feed ratio of H2/CO2 for the conversion and yield in both methanol and DME synthesis in TR, a considerable operation cost is a concern for providing a large concentration of hydrogen gas in the feed. Compared with the conventional reactor, much less H2 is needed to obtain the same DME selectivity in the membrane reactor due to the shifted equilibrium (Poto et al., 2021).

**Sweeping gas flow rate**

In the membrane-assisted catalytic reaction, an increased sweeping gas flow rate not only contributes to the efficient heat removal with a higher heat transfer coefficient but also exerts a positive impact on the performance since the water partial pressure is reduced at the permeation side, resulting in a higher water molar flux and more effective water removal from the reaction (Poto et al., 2021). For example, when the sweeping gas flow rate was increased from 0.06 to 0.6 molCOx h⁻¹, the partial pressure of water at the feed and sweep sides was increased, driving the H2O to transfer via the membrane, thus enhancing the methanol and DME production (Diban et al., 2014). Moreover, a high re-circulation of the sweeping gas effectively reduced the CH3OH driving force and limited the permeation of CH3OH, resulting in a high DME yield up to 30% (Diban et al., 2014). Furthermore, the existence of small amounts of CO or CH3OH in the sweep gas during circulation will inhibit the unwanted permeation from the feed zone (Poto et al., 2021). Although a high sweeping gas flow rate is beneficial, when the flow rate is much higher than that of the reactor inlet (e.g., >5), the absolute effect on the partial pressure of water turned out to be negligible because of the higher water dilution (De Falco et al., 2017). Even worse, in the DRM reaction, although the increased flow rate of sweeping gas enables an improved conversion and H2 yield, a further rise of the flow rate might not be desirable but reduce the conversion of CH4 and CO2 because of the simultaneously inhibited diffusion of reactants and products (Bosko et al., 2010).
Gas hourly space velocity

It is known that a high GHSV value shortens the residence time of reactants and negates the catalytic performances regardless of the reactor (traditional and membrane-assisted types). Also, a high GHSV will diminish the integration benefits of the membrane reactor since the water permeation flux is greatly lowered, which is obviously seen over 60000 h⁻¹ in the DME synthesis. Similarly in the DRM reaction, the conversions of CH₄ and CO₂ were reduced from 62.6% to 26.84% and from 72.6% to 21.57% with the GHSV increasing from 25000 to 97000 mL g⁻¹ h⁻¹ (Liu et al., 2002). To enhance the contact and promote the reaction and diffusion, a low GHSV is preferred. However, the reaction productivity is decreased accordingly. Therefore, a GHSV less than 10000 h⁻¹ might be favored in the DME production so as to maximize the promotional effects of the membrane reactor (De Falco et al., 2017). It is noteworthy that the DME selectivity is always higher in membrane reactors than the traditional counterpart even with a large GHSV value.

In another research, however, the methanol yield was improved with a higher GHSV (Lee et al., 2000). In particular, a high space velocity would maintain the surface oxygen concentration sufficiently small, thus protecting the active center Cu⁺ from being oxidized, leading to a monotonous increase of methanol yield. Even so, an optimal GHSV value is to be explored to alleviate the recycling of the unreacted feed.

CONCLUSIVE REMARKS AND PROSPECTS

In this review, the zeolite-based catalytic membrane reactors and their applications in the thermo-catalytic conversion of CO₂ are comprehensively and critically summarized, mainly including the transport mechanisms in zeolite membranes, synthesis strategies (methods and conditions), surface/structure properties, applications in CO₂ hydrogenations and DRM reaction as well as the impacts of operation parameters on the separation and reaction performances.

As for the synthesis methods, the use of OSDAs as a mineralizing agent and phase controller enables a uniform seed distribution, leading to a thin layer without defects. To avoid the pore blocking by the residues derived from the incomplete OSDA removal, high-temperature calcinations are commonly adopted, which inevitably brings thermal stress and boundary gaps. Mild treatments such as UV and ozone are preferred. Another strategy is to substitute the OSDAs with inorganic SDAs, such as KOH and NaOH. To alleviate the detrimental effect of OH⁻ on the surface area and porosity, fluoride ions can be added to form a synergy. In addition to the OSDA-free method, a gel-free process is helpful for a continuous, thin and oriented zeolite membrane developed from the substrate in situ. In addition, several advanced techniques have been proven successful in synthesizing a high-quality zeolite membrane, including RTP, VAD, high-power ultrasound, and recirculated flow system.

Synthesis conditions also play a crucial role in membrane synthesis. An optimized seed size and concentration benefit a defect-free layer formation. Also, medium concentrations of OH⁻ favor a small size, rapid nucleation, and ordered the alignment of crystals. Besides, by controlling the Si/Al ratios, the surface hydrophobicity/hydrophilicity can be well tuned to satisfy specific applications, such as H₂O permeation or H₂...
separation. In addition, a concentrated gel solution accelerates the nucleation but causes the non-homogeneous size distribution. Moreover, a careful adjustment of the synthesis time benefits a good balance between the thin layer structure and full coverage of support pores. Furthermore, a two-step hydrothermal treatment (low temperature – high temperature) realizes a fast nucleation but a slow crystallization, resulting in a thin and defect-free membrane.

In addition to the synthesis strategies, the surface and structure properties of a well-formed and highly active/robust zeolite membrane are discussed in four categories. First, a thick membrane usually enjoys a dense surface without boundary gaps or cracks, but a thin layer shortens the gas diffusion pathways. To strike a balance, several processing methods such as microwave heating, RTP, and mild treatments are suggested. Second, although diffusivity is higher through the defects, permselectivity is quite limited due to the non-selective permeation through the intercrystalline pores. To address this issue, additives can be added to heal the defects; a support with small pore size is also favored. Notably, the bond formation between crystals is enhanced by RTP, but the cracks are a concern for this treatment method. Third, an ordered orientation of the crystals facilitates gas diffusion. By combining the in-plane and out-of-plane growth of crystals, both diffusivity and permselectivity are improved. Fourth, the affinity to polar or non-polar molecules depends heavily on the surface hydrophobicity and hydrophilicity. With a delicate control of the Si/Al ratio in the precursors, the resulting zeolite membranes can be applied in either CO2 hydrogenation or DRM reactions.

As to the applications of zeolite membranes, the conversion and selectivity are both important factors to be considered in terms of the membrane reactor performance. Also, the catalyst-membrane synergy is better to be formed. By strengthening the metal-support interaction, the dispersion of active sites, sintering resistance, and anti-coking property are all improved, paving the way for the application in harsh condition. In addition, an enhanced affinity to water renders the membrane more H2O-selective and increases the water permeance, thus driving the reaction equilibrium to the targeted products, such as methanol and DME. Moreover, to improve the interaction between the H2-selective membrane and the support, zeolite membranes can be coated to prevent structural collapse and prolong the lifespan. By means of the above modifications, the CO2 adsorption, CH4 activation, H2 permeation, and water diffusion will be increased, thus promoting the CO2 hydrogenations and DRM reaction.

Apart from the modified catalyst and membrane, the operation parameters exhibit a key effect on the catalytic performance of the membrane reactor. Thermodynamically and kinetically, a high temperature favors the DRM, RWGS, and reaction rate, but disfavors the CO2 hydrogenations and catalyst stability. A compromise is necessary for this scenario. As for the pressure, a high value is often favorable due to the large driving force for permeation and equilibrium shift in the reaction. However, a defective membrane might suffer from low selectivity. In addition, the DME selectivity may not be benefited from the high pressure. Furthermore, the concentration of adsorbed H2O molecules could dominate the permeation rather than the partial pressure difference. Similar to the pressure, the impacts of feed ratio (H2/CO2) are complicated. Normally, a high ratio promotes conversion and selectivity, but the considerable operation cost is an issue. Also, the high feed ratio only matters at a low temperature since the temperature effect turns out to be significant when the temperature is higher. For the impacts of sweeping gas flow rate, a high value generally benefits the reaction owing to a larger partial pressure difference. But a further increase of the flow rate might not be useful in CO2 hydrogenations or even bring an adverse influence to the DRM reaction. Finally, a high GHSV reduces the residence time of reactants, thus deteriorating both the permeation and reaction activity; but a low GHSV might harm productivity. Interestingly, a high GHSV can be beneficial to the catalyst stability since Cu+ is well protected from being oxidized in oxygen-deficient atmosphere.

Despite the above progress in the zeolite membranes applied in CO2 conversions, some challenges are still waiting for a solution in the near future.

First, the application of zeolite membranes in thermo-catalytic CO2 conversions is still limited considering the unsatisfactory reproducibility and long-term stability, which is mainly caused by the poor collective orientation of crystals, coke formation at the acidic sites, and support layer properties. The above parameters are still difficult to be precisely controlled in the industrial level. It is imminent to develop more zeolite membranes with thermal and chemical stability in harsh conditions, coke-free surface, and a superior
performance in H₂O or H₂ separation by optimizing the zeolite crystal orientation, surface acidity/basicity, and support properties.

Second, a highly selective and robust catalyst is to be developed for the low-pressure CO₂ hydrogenation and high-temperature DRM reaction. In this scenario, the synergistic effects of the catalyst and zeolite membrane are better exploited. Possibly, realistic mathematical models and advanced in-situ characterizations can be well combined to optimize the catalytic membrane reactor performances.

Third, in CO₂ hydrogenations, certain amounts of water need to be fed so as to block the membrane pores and prevent the loss of reactants, which will reduce the equilibrium yield. An alternative solution is to design the reactor in series where the reaction zone (conventional reactor) is followed by the separation section (membrane reactor).

Fourth, sweeping gas and re-circulation are necessary in both CO₂ hydrogenations and DRM reactions using membrane reactors owing to the enhanced pressure difference and effective heat removal. To realize industrial application, a detailed and accurate evaluation of the technical issues existing in the re-circulation is better conducted. Moreover, a cost analysis regarding the energy input to cool, heat, and compress the sweeping gas streams is necessary.

LIMITATIONS OF THE STUDY
Considering the amounts of zeolite membrane works, especially membrane reactors regarding the CO₂ conversions, no authors are specifically excluded in this review. For the content coverage, this review is mainly focused on the zeolite membrane reactors applied in thermo-catalytic CO₂ conversions, together with the transport mechanisms, synthesis strategies, operation conditions, and intrinsic properties of the zeolite membranes. For other reactions or membrane reactors, please kindly check other review articles.

ACKNOWLEDGMENTS
This research was funded by NUS Green Energy Program (WBS: A-0005323-05-00), FRC MOE T1 (WBS: A-0009184-00-00), A*STAR LCERFI Project (Award ID: U210242011: WBS No. A-8000278-00-00), Guangzhou Basic and Applied Basic Research Project in China: 202102020134; Youth Innovation Talents Project of Guangdong Universities (natural science): 2019KQNCX098.

AUTHOR CONTRIBUTIONS
Conceptualization, data curation, investigation, writing—original draft, X.G., S.D.; writing—review and editing, X.G.; project administration, supervision, validation, S.K.; funding acquisition, resources, S.K. All authors have read and agreed to the published version of the article.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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