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# Recent development on the effect of water/ moisture on the performance of zeolite membrane and MMMs containing zeolite for gas separation; review

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Understanding the effects of water vapour on gas permeation and separation properties of zeolite membranes especially at lower temperatures is important for the applications of these zeolite membranes for gas separations involving water vapour. Zeolite membranes have high potential for the purification of natural gas, biogas and syn-gas to produce the pipe-line gas and often those gases contain moisture. The separation of gases *via* zeolite is quite complex, particularly in the presence of water vapour in the feed stream. The increase of the fluxes of other gaseous components has been reported in some articles while the decrease is reported in the others. As well, both increase and decrease of selectivity are reported. Despite many works conducted during the past 15 years the details on the effect of the water vapour remain unknown. In this paper attempts are made to summarize the results of the experimental investigations with an emphasis on five types of zeolites, e.g. ZSM (MFI), DDR (deca-dodecasil 3R), SAPO-34 (silicoaluminophosphate), FAU (fauzite) and 4A zeolite. As well, interpretation of the experimental observations is attempted based on a simple transport mechanism.

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## Introduction

Gas separation is of vital environmental concern nowadays due to the issue of global climate change. The phenomenon of increasing greenhouse gas concentration, especially carbon dioxide (CO<sub>2</sub>), in the atmosphere has drawn increasing interest among the researchers toward finding efficient methods for CO<sub>2</sub> capture before being emitted to atmosphere. Separation of CO<sub>2</sub> is one such essential step in the natural gas processing plant. Polymeric membranes are widely applied for gas separation in view of their characteristics such as low cost and ease of fabrication into desired gas separator modules. However, their application for gas separation is limited due to the instability at high temperature and occurrence of plasticizing effect in the presence of high CO<sub>2</sub> pressure, which results in reduced CO<sub>2</sub> separation performance of the polymeric membranes. The deficiencies of polymeric membranes have prompted the development of zeolite membranes, which could overcome the problems for CO<sub>2</sub> gas separation.

## Zeolites

The term “zeolite” was originally coined in 1756 by Swedish mineralogist Axel Fredrik Cronstedt, who observed that rapid heating of the material stilbite produced large amounts of steam from water that had previously been adsorbed into the material. Zeolites are microporous, aluminosilicate or silicate minerals. As of November 2010, 194 unique zeolite frameworks have been identified, and over 40 naturally occurring zeolite frameworks are known. Some of the more common mineral zeolites are analcime, chabazite, clinoptilolite, heulandite, natrolite, phillipsite, and stilbite.<sup>1</sup>

Zeolite membranes can be used at high temperatures and with organic solvents, when polymeric membranes cannot operate. Another advantage of thin, supported zeolite membranes is well-defined pores of molecular dimensions. Thus zeolites have great potential to exhibit both high selectivity and high permeability. One of the applications of zeolite membranes is separation of small molecules from gas streams. The latter can be addressed in dehydration of natural gas (NG) in which the water vapour should be removed from the gas stream prior to its entrance to the pipeline. Natural gas contains methane (CH<sub>4</sub>) as the main component, and other impurities such as CO<sub>2</sub>, hydrogen sulfide and water vapour. Water vapour is the most common impurity in natural gas. Separation of water vapour from NG decreases its potential for corrosion,

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hydrate formation and freezing along the pipeline. Among different processes for dehydration of NG, two processes are used at industrial scales including absorption by liquid desiccants and adsorption by solid desiccants.<sup>2</sup>

Generally zeolites are tridimensional microporous crystalline aluminosilicates. The crystalline aluminosilicates consist of Si and Al tetrahedral units ( $\text{TO}_{4/2}$ , where T = Si or Al) linked through bridging oxygen atoms giving rise to the so-called secondary building units (SBUs) that are constituted by rings and prisms of various sizes.<sup>3</sup> These units combine to generate frameworks with a regular distribution of molecular-sized pores and cavities. Zeolites have the chemical formula  $\text{M}_{2/n} \text{OAl}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ , where the charge-balancing nonframework cation M (M cation usually from groups I or II) has valence  $n$ ,  $x$  is 2.0 or more, and  $y$  is the moles of water in the voids.<sup>4</sup>

The Si/Al ratio of the zeolite structure and amount of cations control the surface properties of zeolites (*e.g.*, hydrophobicity and acidity), and determine their adsorbent, catalytic and ion-exchange properties. Pores of zeolites are uniform in sizes determined by their crystal structure.<sup>3,5</sup> Generally, zeolites can be classified into small, medium, large, and ultra large pore materials. Small pore structures have pore apertures consisting of six, eight or nine tetrahedral (6-, 8-, and 9-membered rings), medium pore frameworks have 10-membered rings, large pore zeolites have 12-membered rings, and ultra large structures have 14-, 18- or 20 membered rings.<sup>6</sup>

The possibility of zeolite properties in a membrane configuration is an attractive one, with many potential applications. Their potential molecular sieving action, large surface areas and controlled host-sorbate interactions, especially at low vapour pressure, are the primary motivations in microporous zeolite membranes.<sup>6</sup> Zeolite membranes are completely different from simple zeolite powders.

Zeolite membranes are the microporous inorganic membranes with higher thermal, mechanical and chemical stabilities compared to organic membranes. Its uniform and molecular-sized pore structure with controlled host-sorbate interactions makes it attractive as a shape-selective material for gas separation. Separation of  $\text{CO}_2$  is one such essential step in the natural gas processing plant. Natural gas, biogas, syn-gas contain water and water absorbs in zeolite. Synthesis gas produced from biomass usually contains more  $\text{CO}_2$  than desired, and it also contains hydrogen sulphide and moisture/water. It is necessary to study the effect of water/moisture on  $\text{CO}_2$  separation by zeolite membrane when the pipeline gas is produced from natural gas, biogas or syn-gas. The effects of water vapour on gas permeation and separation properties of zeolite membranes are important to the applications of these zeolite membranes for separation involving water vapour. It is well known that water/vapour lowers  $\text{H}_2$  and  $\text{CO}_2$  permeation especially at low temperature.

The decrease in  $\text{H}_2$  permeance could be attributed to the adsorption of water vapour and blocking of zeolite pores. This phenomenon should be more significant at lower temperature where the mobility of  $\text{H}_2\text{O}$  molecules decreases and the amount of adsorbed  $\text{H}_2\text{O}$  molecules increase due to the stronger interaction.

At high temperatures, the interaction between water vapour and surface material causes the densification or damage of pore structure, while at low temperatures, the permeance decreases significantly due to the presence of water vapour, even without destroying the pore structure.<sup>5,7</sup>

It was observed that the transport of gas through zeolite membrane as a function of temperature goes through a maximum, then decreases, and rises again at higher temperature.<sup>8</sup> The separation *via* zeolite membrane is based on molecular size and polarity among others. Molecules with higher molecular weight permeate better at low temperature while at high temperature lighter molecules show better permeability. This is the reason why  $\text{H}_2$  permeates better at higher temperatures (about 500 °C) while  $\text{CO}_2$  does at lower temperature. In general these membranes show high permeability and low selectivity.<sup>9</sup>

The particular affinity a species to an internal zeolite cavity depends on electronic considerations. The strong electrostatic field within a zeolite cavity results in very strong interaction with polar molecules such as water. Non-polar molecules are also strongly adsorbed due to the polarizing power of these electric fields. Thus, excellent separations can be achieved by zeolites even when no steric hindrance occurs.<sup>10</sup>

The structure and chemistry of support materials also play an important role in zeolite membrane formation and have a significant influence on the separation property of the membrane material. Surface roughness and pore size define the optimum zeolite crystal size and membrane thickness. The chemical nature of the support surface influences zeolite nucleation, crystal growth and membrane adhesion. It has been demonstrated that chemical modification of the support surface can significantly alter the zeolite membrane formation.<sup>11</sup>

The separation of a gas mixture by zeolite is affected by:<sup>12</sup>

- (1) Size or steric exclusion of certain components of a gas mixture prevents them from entering the zeolite pores, whereas the other components enter the pores and are adsorbed.
- (2) Thermodynamic selectivity, which is a quantitative measure of the preferential adsorption of certain components over others when all components can enter the pores.
- (3) Kinetic selectivity, which is a quantitative measure of the ability of certain components to enter the pores (and become adsorbed) faster than other components.

The suppression effect of an adsorbing component on the permeation of a non-adsorbing component is well known for zeolite membranes.<sup>13</sup> Several articles on the suppression effect of water vapour on gas permeation in MFI membrane at low temperatures have been reported in literature.<sup>14–16</sup> Aluminum atoms in the zeolite framework significantly affect the physicochemical properties of zeolites. Water molecules adsorb on zeolite surface through dipole-field interactions as well as hydrogen bonds with residual hydroxyl groups.<sup>17</sup> The number of the latter also depends on the population of Al atoms in the framework. Therefore, the affinity of zeolites with water molecules depends on their Si/Al ratio.<sup>18,19</sup> During the last fifteen years the effect of water/moisture on the separation of gases *via* zeolite membranes, mainly ZSM (Zeolite Socony Mobil-5) (MFI),

SAPO-34 (silicoaluminophosphate), DDR (deca-dodecasil 3R), and FAU (fauzsite) has been reported.

Calero and Gómez-Alvarez<sup>18</sup> made detailed studies of the H bonded structure of water adsorbed in zeolites using Monte Carlo simulation with validated atomistic descriptions and intermolecular interactions. The calculated hydrogen bonding properties were in close relation to the adsorption behavior. The adsorption mechanism proceeds through nucleation of water molecule in zeolite. At saturated states, it was proved by simulations that water is significantly perturbed from its bulk behavior. More extended and complex hydrogen bonding networks were found in FAU and MFI zeolites.

A number of methods have been reported for the preparation of zeolite membranes. These methods are generally differing in the pre-treatments of the stable or temporary supports, impregnation techniques for these supports, or in their post-synthesis treatments. In principle, synthesis mixtures characterized by high percentages of water and low alkalinity are optimal for the preparation of the zeolitic membranes.<sup>6</sup> It is well known that the process for the preparation of membranes affects the performance of finished membranes. Zeolite membranes were often prepared in conditions similar to zeolite powder synthesis. Several methods for the synthesis of zeolite membranes have been developed in order to control the thickness of the membrane, compactness, and orientation of atoms or molecules. Beside these properties, the hydrophilic/hydrophobic nature of zeolites can be tuned by changing the Si/Al ratio in the framework of zeolites. In general all methods described in the literature involve either the use of zeolite crystals previously synthesized or the crystallization of zeolite layers. Zeolite membranes are usually prepared by *in situ* hydrothermal synthesis on porous stainless steel, alpha-alumina, or alpha-alumina support tubes or disks for the gas permeation studies.

There are many methods for the preparation of zeolite membranes which are as follows:<sup>19–24</sup>

(1) Embedded method: Barrer and James<sup>25</sup> were the first to fabricate zeolite membranes in which microcrystalline ion-exchanging zeolites are bonded by inert polymeric fillers in such a way that the electrochemical behavior is determined by the crystals and by crystal contacts. The embedded method is not a good choice as in the final membrane there will be many defects and the performance is not reliable.

(2) *In situ* hydrothermal synthesis method: this method is commonly used. In this method bring a porous support in direct contact with the synthesis solution or gel, and then to allow the growth of a zeolite film on the surface of the support under hydrothermal conditions. The formation of the zeolite membrane under hydrothermal conditions involves the formation of the supersaturation region adjacent to the substrate surface, nucleation, aggregation, crystallization and crystal growth.

(3) Seeding technique (secondary growth method): to enable better control of nucleation and crystal growth steps, seeding technique is better than other techniques. In this method, first a colloidal zeolite suspension of sub- $\mu\text{m}$ -sized seed crystals prepared. These crystals will be coated as a seed layer on the

surface of the substrate. Hydrothermal synthesis is followed to grow zeolite film on the seed layer. The preparation of zeolite sol as crystal seeds is the key step in the secondary method.

(4) Microwave method: the microwave method for the preparation of zeolite membranes is similar to the conventional hydrothermal method except that the autoclave is placed in a microwave field. The synthesis time reduce greatly.

(5) DGC method was first proposed by Xu *et al.*,<sup>26</sup> which is a novel method to synthesize zeolite membrane on porous supports. The zeolite ZSM-5 has been synthesized from amorphous aluminosilicate gels in a vapour of ethylenediamine, triethylamine, and water. DGC has the benefit of better thickness control compared with liquid phase synthesis, since the amount of nutrient for growing zeolite is directly controlled by the amount of gel applied.

Hedlund *et al.*<sup>27,28</sup> discussed a method to prepare an ultra-thin (less than 1  $\mu\text{m}$ ) membrane without defects on an open support.

### ZSM/MFI

ZSM-5, Zeolite Socony Mobil-5, (framework type MFI from ZSM-5) is an aluminosilicate zeolite belonging to the pentasil family of zeolites. Its chemical formula is  $\text{Na}_n\text{Al}_n\text{Si}_{96-n}\text{O} \cdot 16\text{H}_2\text{O}$  ( $0 < n < 27$ ). Several articles are reported on the suppression effect of water vapour on gas permeation in MFI zeolite membranes at low temperature (<572 K).<sup>11,12</sup> Gas permeation through MFI zeolite membranes in the presence of water vapour at high temperatures (above 300 °C) is technically important to apply MFI zeolite membranes for chemical reactions and separation involving water vapour, such as water gas shift reaction for hydrogen production.<sup>29</sup>

Highly siliceous ZSM-5 zeolites with low  $\text{Al}_2\text{O}_3$  content are known to have highly hydrophobic surfaces.<sup>30</sup> It is well known that the surfaces of the siliceous zeolites (*e.g.*, silicalite, dealuminated mordenite, USY-zeolites) show higher hydrophobic properties than  $\text{Al}_2\text{O}_3$ -containing zeolites.<sup>31</sup> Takeuchi *et al.*<sup>32</sup> studied the adsorption of the water molecules on various ZSM-5 zeolites (different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, Table 1).

HZSM zeolite ( $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 1880), with a low  $\text{Al}_2\text{O}_3$  content, exhibited the highest hydrophobicity among the ZSM-5 zeolites with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios. As the  $\text{Al}_2\text{O}_3$  content increased to *ca.* 4 wt%, corresponding to a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 23.8, the amount of  $\text{H}_2\text{O}$  adsorbed increased three fold more than the highly siliceous H-ZSM-5 (1880).<sup>32</sup> Desorption of the  $\text{H}_2\text{O}$  molecules can be seen at 373–573 K for H-ZSM-5 zeolites with low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of 23.8 and 68. However, very small amounts of  $\text{H}_2\text{O}$  desorbed from H-ZSM-5 with low  $\text{Al}_2\text{O}_3$  content ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 220$  and 1880). Moreover, as the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio

Table 1  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of various ZSM-5 zeolite<sup>32</sup>

Zeolite	$\text{SiO}_2/\text{Al}_2\text{O}_3$
ZSM-5	1880
H-ZSM	220
H-ZSM-5	68

decreased, the desorption temperature shifted slightly toward higher-temperature regions. Generally, H<sub>2</sub>O molecules weakly adsorb on surface hydroxyl groups by the hydrogen bonds and strongly adsorb on the cationic sites of oxide surfaces by electrostatic interactions. Maybe this phenomenon is also true for other zeolites.

A detailed study of the effect of moisture on the CO<sub>2</sub>/N<sub>2</sub> permeation and separation performance of Mobile Five (MFI) zeolite membranes was done by Sublet *et al.*<sup>33</sup> At high water concentrations, beyond the value at which capillary condensation occurs in small mesoporous defects, MFI membranes show the gas permeance reduction of about 40% at the steady state when the water concentration is 10 v/v% at 373 K. The incorporation of water promotes however CO<sub>2</sub>/N<sub>2</sub> separation factors, most probably due to defective pore blockage and formation of bicarbonate stable intermediates. The CO<sub>2</sub> permeation and separation properties of nanocomposite MFI-alumina membranes in the presence of water, combined with their hydrothermal stability and optimal reproducibility, make these materials potentially competitive for post combustion CO<sub>2</sub> capture applications, compared with other zeolite membrane materials (*e.g.*, FAU-type membranes).

Hill and Seddon<sup>34</sup> investigated the hygroscopic nature of H-ZSM-5 and reported that under ambient conditions the zeolite H-ZSM-5 contains 7–9% water and anhydrous zeolite can be obtained by prolonged heating over 200 °C (473.1 K). On the other hand, silicates typically contain much less water (around 1%) under ambient conditions. The sorption of water into H-ZSM-5 obeys Henry's law. The surface of the zeolite is hydrophilic, and water is able to displace hydrocarbon from the surface. Moreover sorption of water inside the channels requires the presence of acid centers which can break up surface bound water. The apparent anhydrous nature of silicates is seen as a result of surface bound water being unable to penetrate the channels because of hydrogen bonding between water moieties and the hydrophilic surface favors the structuring of the adsorbed water and militates against individual water molecules diffusing down the channels. The very strong desorption of water on the zeolites is caused by interaction of the permanent and large dipole moment of water with a zeolite cation. The Henry's law constant for adsorption of water on KA zeolite is much larger than that for the NaX zeolite due to the smaller cavity of the A zeolite and the higher charge density of the K ion.

Chen<sup>30</sup> hypothesized the role of defects to the water adsorption and studied adsorption of water vapour gravimetrically in mordenite type zeolites from pressure ranging from vacuum to saturation. It was reported by Chen that each additional alumina site allowed for a coordination (or adsorption) of four molecules of water. Matsukata *et al.*<sup>15</sup> studied the effect of water adsorption on MFI-type zeolite during the permeation of H<sub>2</sub>, *n*-C<sub>4</sub>H<sub>10</sub> and equimolecular mixed gas H<sub>2</sub>/*n*-C<sub>4</sub>H<sub>10</sub>. It was observed that the permeation properties of a MFI-type zeolite membrane were influenced by the water adsorbed in the membrane. Even 500 ppb water stream influences the single gas permeation properties of the membrane. These properties of the membranes might be caused by strong hydrophilicity of

highly aluminated MFI-type zeolite formed in the *in situ* crystallization method.

Noack *et al.*<sup>14</sup> studied the water vapour permeation fluxes through MFI zeolite membranes with different Si/Al ratios at low temperatures 378 K (105 °C). In pervaporation and steam permeation measurements of water/iso-propanol and water/methanol mixtures, the silicate membrane showed a hydrophobic and the ZSM-5 membrane a hydrophilic separation behavior. Funke *et al.*<sup>35</sup> found no permanent effect of water vapour on the pure gas permeation performance of ZSM-5 membranes. Though the pure N<sub>2</sub> and SF<sub>6</sub> permeances decreased after humidification of the feed stream (61% for N<sub>2</sub> and 16% for SF<sub>6</sub>), the initial values were recovered after water removal.

Bernal *et al.*<sup>36</sup> investigated the separation of equimolecular CO<sub>2</sub>/N<sub>2</sub> saturated with water vapour at room temperature using B-ZSM-5 membrane. The CO<sub>2</sub> permeation fluxes decreased about 54% and 29% for feed pressure of 1.7 and 2.2 bars, respectively, while the temperature of the membrane were increased from 300 K to 473 K. The existence of water in the feed did not change the separation factor significantly, even at low temperatures. In summary, the effect of humidity was small, due to the limited hydrophilicity of ZSM-5 membranes.

Shin *et al.*<sup>37</sup> studied ZSM-5 zeolite membranes for CO<sub>2</sub> separation from CO<sub>2</sub>/N<sub>2</sub> mixture. ZSM-5 membranes were synthesized *via* hydrothermal-treating of various porous  $\alpha$ -alumina tubes in template reaction mixtures. The ZSM-5 zeolite membranes were evaluated by the CO<sub>2</sub>/N<sub>2</sub> separation factor and permeance measured as a function of the stage cut, the helium sweeping rate, the feed pressure, and the permeation temperature. The maximum separation factor of the ZSM-5 zeolite membrane for a CO<sub>2</sub>/N<sub>2</sub> (50% CO<sub>2</sub>) gas mixture was about 54.3 at 25 °C and its permeance was  $3.6 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ . Fig. 1 shows the separation factor of the ZSM-5 zeolite membrane in moisture-saturated feed gas system. Separation

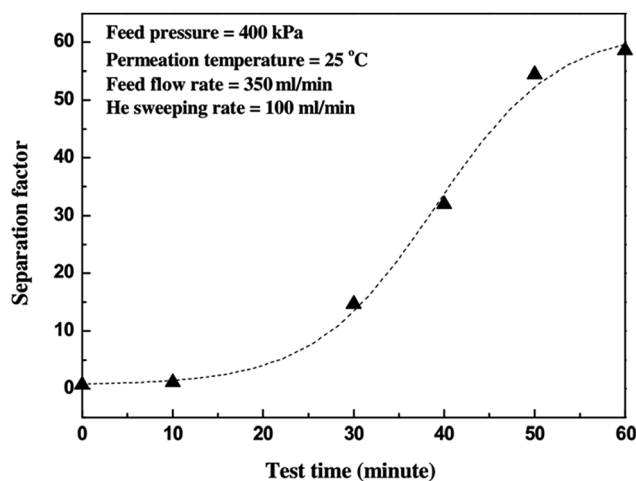


Fig. 1 CO<sub>2</sub>/N<sub>2</sub> separation factor vs. gas permeation test time for the surface modified ZSM-5 zeolite membrane in the moisture-saturated feed gas system. Reproduced from ref. 37 with permission from the Elsevier.

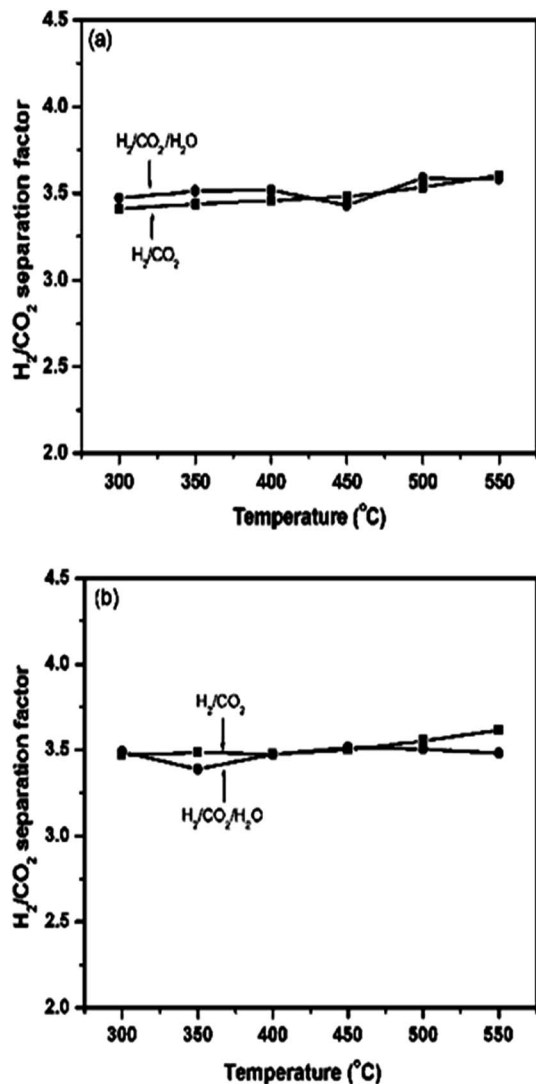


Fig. 2 H<sub>2</sub>/CO<sub>2</sub> separation factor with equimolar H<sub>2</sub>/CO<sub>2</sub> binary mixture (square) and H<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O ternary mixture (circle) as feed for silicate (a) and ZSM-5 zeolite (b) membranes. Reproduced from ref. 38 with permission from the John Wiley and Sons.

factor increases as the permeation test time increases. In presence of humid gas, selectivity went down to even less than 1. With the increase in experiment time, the selectivity increased with time and reached >50, which was almost the same as obtained with dry feed. Shin *et al.* suggested that at the beginning, permeate N<sub>2</sub> flow is more than CO<sub>2</sub> flow because CO<sub>2</sub> adsorption on the zeolite pore wall was hindered by moisture. As the permeation time increases, moisture occupies the large pores through which N<sub>2</sub> flows mainly. In these circumstances the flow of nitrogen decreased. Fig. 1 shows that after 50 min experiment time, the CO<sub>2</sub>/N<sub>2</sub> separation factor in moisture-saturated feed gas system is slightly higher (<55) than that in dry feed gas system (around 55). It is possible because ZSM-5 zeolite has a high hydrophobic quality.

It was suggested by Shin *et al.*<sup>37</sup> that the permeation of CO<sub>2</sub> through ZSM-5 zeolite membranes was mainly governed by both mechanisms of the adsorption/surface diffusion and the

activated micropore diffusion, while that of N<sub>2</sub> was governed by the activated micropore diffusion only.

Wang and Lin<sup>38</sup> studied the effects of water vapour on H<sub>2</sub> and CO<sub>2</sub> permeation and separation properties of ZSM-5 (Si/Al ~ 80) zeolite and aluminum free silicalite membranes. The experiments were carried out with equimolar H<sub>2</sub>/CO<sub>2</sub> binary and H<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O ternary mixtures at temperatures 300–550 °C. Fig. 2 shows the temperature dependence of selectivity. The H<sub>2</sub>/CO<sub>2</sub> separation factor for the mixture with and without water vapour is essentially the same for both membranes indicating that the presence of water vapour suppresses gas permeation for H<sub>2</sub> and CO<sub>2</sub> to the same extent. It suggests that at high temperatures water vapour has the same effects on lowering the permeation rate of other gases, regardless of gas type and zeolite surface-gas molecular gas interactions.

Wang and Lin<sup>38</sup> also reported that both ZSM-5 and aluminum-free silicalite membranes adsorb water vapour even at temperatures in the range of 572–782 K and reduce the permeability of H<sub>2</sub> and CO<sub>2</sub> in the pores of zeolite membranes. It was also reported that water vapour exhibits negligible effects on gas permeation through silicate membranes at even high temperatures (>822 K). The suppression effect of water vapour on H<sub>2</sub> and CO<sub>2</sub> permeation was larger for the less hydrophobic ZSM-5 zeolite membrane than for the hydrophobic silicate membrane. For both membranes the suppression effect was stronger at lower temperatures and higher water vapour partial pressures.

Lindmark and Hedlund<sup>39</sup> studied the CO<sub>2</sub> removal from CO<sub>2</sub>/H<sub>2</sub> in absence of water and in presence of water at the temperatures between 22 and 150 °C using MFI membranes. Different types of MFI membranes (LiZSM-5, BaZSM-5) were used and they were prepared from NaZSM-5. It was observed that the Si/Al ratio and the counter ions in the membrane had a significant effect on both single gas permeation and mixture separation by modifying both the effective pore size and the adsorption properties of the membrane. Three feed system (Table 2) were used to study the water/moisture effect on the performance of MFI membranes for the separation of CO<sub>2</sub>/H<sub>2</sub> mixture.

Fig. 3 shows the results of experiments with feed A. The binary CO<sub>2</sub>/H<sub>2</sub> permeances (a) and separation factors (b) for a silicalite-1 membrane (S1) and three ZSM-5 membranes with different counter ions (LiZ1, NaZ1 and BaZ1) are shown. Even though adsorbed CO<sub>2</sub> is not expected to block the permeation of hydrogen significantly, or *vice versa*, the hydrogen and CO<sub>2</sub> permeances at 25 °C are 5–6 times lower than the permeances observed in single gas measurements at the same temperature. This is probably explained by a combination of concentration

Table 2 Compositions of the three feeds used in the separation experiments. The partial pressure of each component (kPa) is given in the table<sup>39</sup>

Feed	CO <sub>2</sub>	He	H <sub>2</sub>	H <sub>2</sub> O
A	50.65	50.65	—	—
B	—	49.6	49.6	2.1
C	49.6	49.6	—	2.1

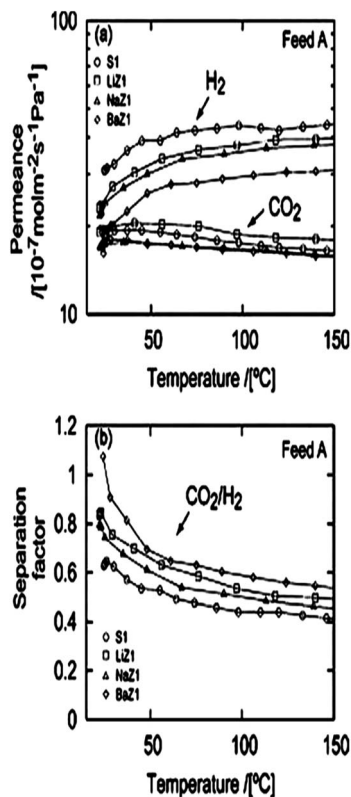


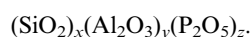
Fig. 3 Binary CO<sub>2</sub>/H<sub>2</sub> permeances (a) and separation factor (b) for a silicalite-1 membrane (S1) and three ZSM-5 membranes with different counter ions (LiZ1, NaZ1 and BaZ1). The feed consists of 50.65 kPa H<sub>2</sub> and 50.65 kPa CO<sub>2</sub>. Sweep gas, He at 1000 ml min<sup>-1</sup> and atmospheric pressure. Reproduced from ref. 39 with permission from the Elsevier.

polarization and back diffusion of helium from the sweep gas in the mixture separation experiments. The hydrogen permeance is lowest at 22 °C and increases by a factor of 1.5–2.0 with increasing temperature up to 150 °C for all membrane types.

Fig. 4 shows the results of experiments where B was used as feed. Only the binary H<sub>2</sub>O/H<sub>2</sub> permeation and separation factor are shown as the function of temperature. The hydrogen permeance is about 5–6 times lower in the presence of water (feed B) than in the presence of CO<sub>2</sub> (feed A), as suggested by Lindmark and Helund<sup>39</sup> it is possible that water is blocking the permeation of hydrogen quite effectively, whereas CO<sub>2</sub> seems to block hydrogen permeance to a minor extent. As the adsorption of water decreases with increasing temperature, hydrogen permeance increases.

#### SAPO-34 (silicoaluminophosphate)

The crystal structure of SAPO, a micro pore zeolite, is similar to that of chabazite and has a special water absorbing capacity. Its formula is



Thermogravimetric studies on the adsorption of water on SAPO-34 powder have shown that significant adsorption only

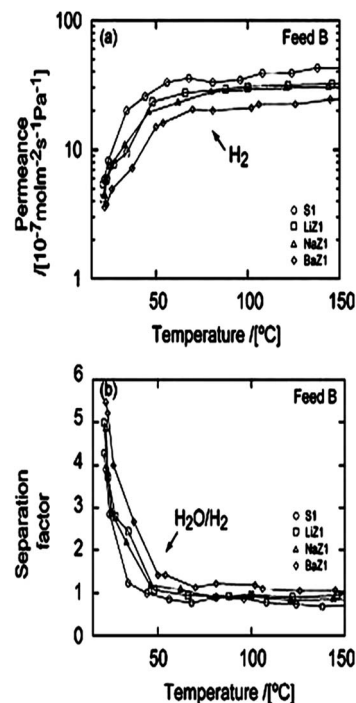


Fig. 4 Binary H<sub>2</sub> permeance (a) and H<sub>2</sub>O/H<sub>2</sub> separation factor (b) for a silicalite-1 membrane (S1) and three ZSM-5 membranes with different counter ions (LiZ1, NaZ1 and BaZ1). The feed consists of 49.6 kPa H<sub>2</sub>, 49.6 kPa He and 2.1 kPa H<sub>2</sub>O. Sweep gas, He at 1000 ml min<sup>-1</sup> and atmospheric pressure. Reproduced from ref. 39 with permission from the Elsevier.

occurs below 373 K, and heating above this temperature is sufficient to desorb most of the water.<sup>40</sup> Poshusta *et al.*<sup>41</sup> fabricated a SAPO-34 (silicoaluminophosphate) membrane and noted a CO<sub>2</sub>/CH<sub>4</sub> separation factor of 30 at 300 K and 4.7 at 470 K. They also reported the effects of water content on gas permeation and suggested that adsorbed water appeared to completely block the SAPO pores, but permeation through non-SAPO pores increased with water content. Further, Poshusta *et al.*<sup>42</sup> investigated the effects of humidity on gas permeation of five SAPO-34 membranes synthesized by the same procedure, but their initial properties were different. These differences could be due to uncontrollable factors in the synthesis (*e.g.* support defects, dust in the synthesis solution, and stress fractures in the membrane) or humidity induced changes in the membranes between the initial calcination and when the first permeances were measured. The effect of water on single gas permeances depends on membrane quality.

Membranes with high CO<sub>2</sub>/CH<sub>4</sub> separation selectivities (>20) were stable in humidified gases, but degradation was seen for some membranes after months of exposure to the laboratory atmosphere. Once the membranes started to degrade, the rate of degradation appeared to accelerate. The degradation created non-SAPO pores that were larger than the SAPO-34 pores, as noticed by i-C<sub>4</sub>H<sub>10</sub> permeance. The effect of humidity on gas permeance correlated with these indicators of non-SAPO pores. Adsorbed water appeared to completely block the SAPO pores, but permeation through non-SAPO pores increased with

humidity. It was concluded by Li *et al.*<sup>43</sup> that water adsorption can be used to determine membrane quality and the fraction of transport through non-SAPO pores. The CO<sub>2</sub> recovered the original permeances and selectivity after calcination at 573 K for 24 h.<sup>43</sup> Water had a strong effect on gas permeation through SAPO-34 membranes. An important drawback of silicoaluminophosphates was their hydrophilicity and, as a consequence, low stability under humid conditions.<sup>44</sup> Thus, the separation performance of SAPO-34 membranes is greatly disturbed by the presence of water<sup>42</sup> and reported that CO<sub>2</sub> flux and selectivity decrease in the presence of water since water has a strong affinity to the hydrophilic SAPO-34 membrane. Therefore, hydrophobic narrow pore zeolite membranes are more appropriate to separate CO<sub>2</sub> from humid gases. Consequently DDR membranes show high CO<sub>2</sub> flux and selectivity and an only negligible water influence on the separation performance in the CO<sub>2</sub> separation from natural gas<sup>45,46</sup> as shown below.

### DDR type zeolites

Among the various zeolite materials, DDR (Deca-dodecasil 3R) is a pure silica (SiO<sub>2</sub>) zeolite. The pore system comprises relatively large (19-hedral) cages interconnected through 8-ring windows with aperture approximately 3.6 × 4.4 Å. Due to its relatively small pore size, DDR can be used to separate light gases, such as CO<sub>2</sub> (kinetic diameter = 3.3 angstroms) from CH<sub>4</sub> (diameter = 3.8 angstroms). Other advantages of DDR zeolites include high thermal stability and chemical resistance due to the pure silica composition. Zeolite DDR can be synthesized from various precursor materials and methods in the temperature range 363–473 K for periods of time between several hours to several weeks in autoclaves with different sol composition.

Five new methods for synthesizing DDR zeolite nanocrystals (200–2000 nanometers in size) are disclosed using hydrothermal secondary growth (seeded growth). By changing the ratio of silica to water, the synthesis temperature, and the mineralizing agents, the morphology and size of the crystals can be manipulated.<sup>1</sup>

DD3R membrane showed high selectivity of CO<sub>2</sub> over methane. The DD3R zeolite is also considered suitable for use in separation of biogases in which moisture is abundant.<sup>2</sup> The permeation and separation characteristics of light gases through DD3R membranes can be explained by taking into account: (1) steric effects introduced by the window opening of DD3R leading to molecular sieving and activated transport, (2) competitive adsorption effects, as observed for mixture involving strongly adsorbing gases, and (3) interaction between diffusing molecules in the cages of the zeolite.<sup>47</sup> DDR type zeolite is essentially comprised of silicon and oxygen atoms, and is expected to be affected less by water adsorption.

The effects of H<sub>2</sub>O on CO<sub>2</sub>/CH<sub>4</sub> separation were investigated for DDR type zeolite membranes by Himeno *et al.*<sup>48</sup> The system was maintained at a steady state with a CO<sub>2</sub>/CH<sub>4</sub> mixture at 298 K for 4 h; a CO<sub>2</sub>/CH<sub>4</sub> mixed gas that contained water vapour was then introduced to the feed. The CO<sub>2</sub> permeance through the DDR-type zeolite membrane decreased rapidly from 2.5 × 10<sup>-7</sup> mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup> to 1.1 × 10<sup>-7</sup> mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>, although the

CH<sub>4</sub> permeance was almost equal to that for a dry mixture gas. The CO<sub>2</sub>/CH<sub>4</sub> separation selectivity decreased to half that of the dry CO<sub>2</sub>/CH<sub>4</sub> mixture. However, the CO<sub>2</sub> permeance and CO<sub>2</sub>/CH<sub>4</sub> selectivity were restored rapidly afterward when dry gas mixture was introduced. The CO<sub>2</sub> permeance and the CO<sub>2</sub>/CH<sub>4</sub> selectivity with saturated water vapour were retained respectively as 1.1 × 10<sup>-7</sup> mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup> and 100.

Tomita *et al.*<sup>45</sup> fabricated the molecular-sieve DDR type zeolite membrane with an aperture of 0.36 × 0.44 nm on a porous alumina substrate by hydrothermal process and studied the performances for CO<sub>2</sub>/CH<sub>4</sub> separation in presence of water. At 301 K the permeance of CO<sub>2</sub> decreased from 7 × 10<sup>-8</sup> mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup> in the dry mixed gas feed to 4 × 10<sup>-8</sup> mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup> in the mixed gas feed with 3.3% water. The separation factors of dry and wet gas feed were 280 and 330, respectively. On the other hand, at 373 K the permeance was 4 × 10<sup>-8</sup> mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup> and the separation factor was 120. No changes were observed between dry and wet gas feed. It was suggested by Tomita *et al.*<sup>45</sup> that water adsorbed into the micropores and blocked the gas permeation of both CO<sub>2</sub> and CH<sub>4</sub> at 301 K to some extent, while at 373 K little effect of water adsorption on the gas permeation was noticed. The DDR type zeolite membrane consists only of silicon and oxygen atoms and is classified as hydrophobic among other zeolites. It was suggested by Tomita *et al.* that DDR type zeolite membrane is not perfectly hydrophobic as they observed some water adsorption effects at 301 K. It was concluded by Tomita *et al.*, that DDR type membranes worked as molecular-sieving membrane. Himeno *et al.*<sup>48</sup> reported a comprehensive study on high-quality DD3R membrane, pointing out a remarkable decrease of CO<sub>2</sub> permeance (*ca.* 40%) in the presence of a moisture saturated stream, the CO<sub>2</sub>/CH<sub>4</sub> separation factor being enhanced about 50%.

Himeno *et al.*<sup>48</sup> also studied the adsorption isotherm of water vapour on DD3R crystal. Fig. 5 shows the adsorption isotherm of water vapour on DD3R crystal at 298 K.<sup>47</sup> The upper limit of

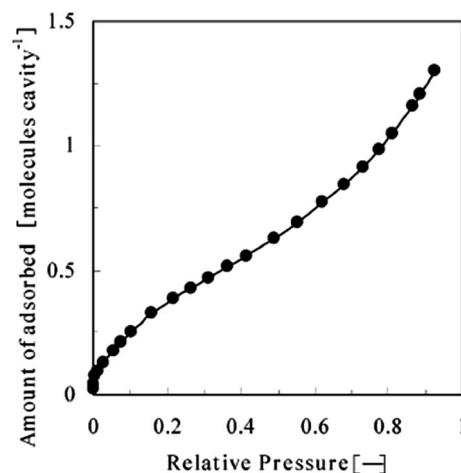


Fig. 5 Adsorption isotherm of water vapour on a DDR crystal at 298 K. Reproduced from ref. 48 with permission from the Royal Society of Chemistry.

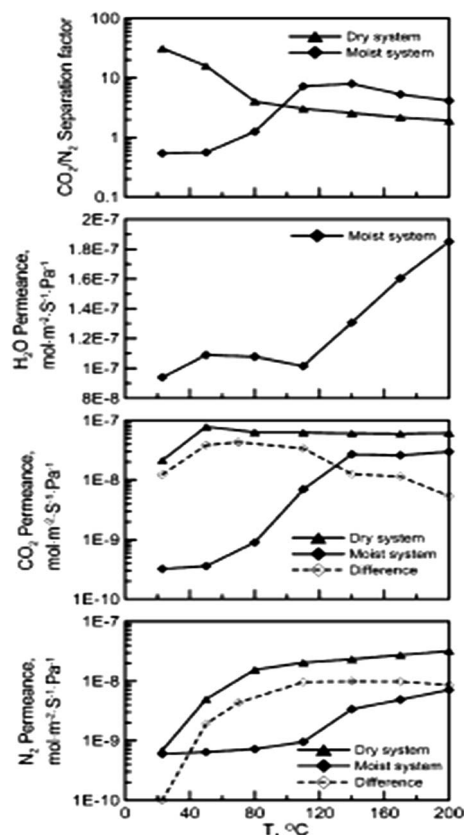


Fig. 6 Gas permeance and  $\text{CO}_2$  factor as functions of temperature for equimolar  $\text{CO}_2/\text{N}_2$  mixtures under dry and moist conditions. Reprinted with permission from<sup>55</sup> American Chemical Society.

the relative pressure of water vapour was 0.92, and the maximum amount adsorbed was  $\sim 19 \text{ mg g}^{-1}$  at 298 K at a water vapour pressure of 2.93 kPa. The maximum amount of adsorbed water vapour was compared to the accessible volume of the intra-crystalline space of the DDR. The accessible volume was estimated to be  $0.14 \text{ ml g}^{-1}$ , using liquid nitrogen adsorption, and the degree of volume filling was 0.13. A unit cell of DDR is comprised of six decahedra, nine dodecahedra, and six 19-hedra. Only the 19-hedra can adsorb adsorbate molecules.<sup>49,50</sup> 19-Hedron cage can theoretically accommodate around 10 water molecules. The number of adsorbed water molecules per 19-hedron cage was around 1. Therefore, water vapour was considered to influence permeation through DDR-type zeolite membranes only slightly. Indeed, the DDR-type zeolite membranes are only slightly affected by water vapour: the  $\text{CO}_2$  permeance and the  $\text{CO}_2/\text{CH}_4$  selectivity with saturated water vapour at 298 K remained  $1.1 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  and 100, respectively.

### FAU type zeolite

Studies were made on  $\text{CO}_2$  removal from low pressure flue gas using naturally occurring zeolites such as X and Y faujasite systems<sup>51</sup> including synthetic zeolites such as 5A and 13X.<sup>52</sup> Faujasite has a 3-dimensional pore structure with pores running perpendicular to each other in the  $x$ ,  $y$ , and  $z$  planes

similar to LTA and has a void volume fraction of 0.48, with a Si/Al ratio of 2.43. Gu *et al.*<sup>53</sup> prepared FAU (Y-type) zeolite membranes by secondary growth of NaY seed layers on alpha alumina substrate and studied the separation of dry and humidified  $\text{CO}_2/\text{N}_2$  mixtures. The separation results for the dry and humid  $\text{CO}_2/\text{N}_2$  mixtures are shown in Fig. 6. With the humidified  $\text{CO}_2/\text{N}_2$  mixture, the permeance values of all three components, including  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{N}_2$ , increased with the temperature in the entire tested range, while  $\alpha_{\text{CO}_2/\text{N}_2}$  experienced a maximum at about  $140 \text{ }^\circ\text{C}$ . At room temperature, the  $\text{CO}_2$  selectivity was about 31.2 for  $\text{CO}_2/\text{N}_2$  dry gas mixture with a  $\text{CO}_2$  permeance of  $2.1 \times 10^{-8} \text{ mol m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$ . The addition of water vapour to the feed stream decreased the performance for both  $\text{CO}_2$  and  $\text{N}_2$  in a temperature range of  $23\text{--}200 \text{ }^\circ\text{C}$ . In presence of water vapour the selectivity was increased in the  $110\text{--}200 \text{ }^\circ\text{C}$  range. On the other hand the selectivity of  $\text{CO}_2$  drastically reduced below  $80 \text{ }^\circ\text{C}$ . In the entire range of tested temperature, both  $\text{CO}_2$  and  $\text{N}_2$  permeance of the moist mixture were below those for the dry mixture due to the adsorbed  $\text{H}_2\text{O}$  molecule as it reduced the zeolite pore volume.

The results of  $\text{CO}_2$  separation at  $200 \text{ }^\circ\text{C}$  are shown as a function of the water partial pressure in Fig. 7. At  $200 \text{ }^\circ\text{C}$ , with increasing water partial pressure, the  $\text{CO}_2$  selectivity showed a maximum of 4.6 at water partial pressure of 12.3 kPa. It was explained by the closure of the zeolite pore at high water partial pressure, which limited the entry and transport of  $\text{CO}_2$  molecules. The  $\text{N}_2$  permeance barely changed while the  $\text{CO}_2$  permeance continued to drop after  $\alpha_{\text{CO}_2/\text{N}_2}$  reached the maximum, suggesting that  $\text{N}_2$  permeation was mainly through large intercrystal pores.

Sawamura *et al.*<sup>54</sup> demonstrated that FAU zeolite membranes have superior stability in comparison with a conventional LTA-type zeolite membrane in a separation of mixture containing large water content. Shirazian and Ashrafzadeh<sup>55</sup> studied the water vapour and methane permeation through NaA zeolite membrane. Zeolite NaA seeds for preparation of membranes were synthesized using hydrothermal treatment. NaA membranes were also prepared *via* secondary growth method on porous alpha alumina as substrate. The results showed that increasing the temperature enhances the permeation of water

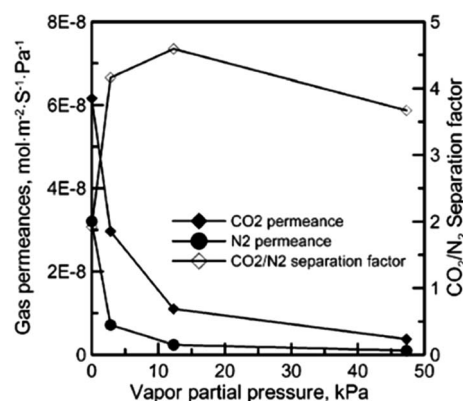


Fig. 7 Effect of the water partial pressure on  $\text{CO}_2/\text{N}_2$  separation at  $200 \text{ }^\circ\text{C}$ . Reprinted with permission from ref. 53 American Chemical Society.



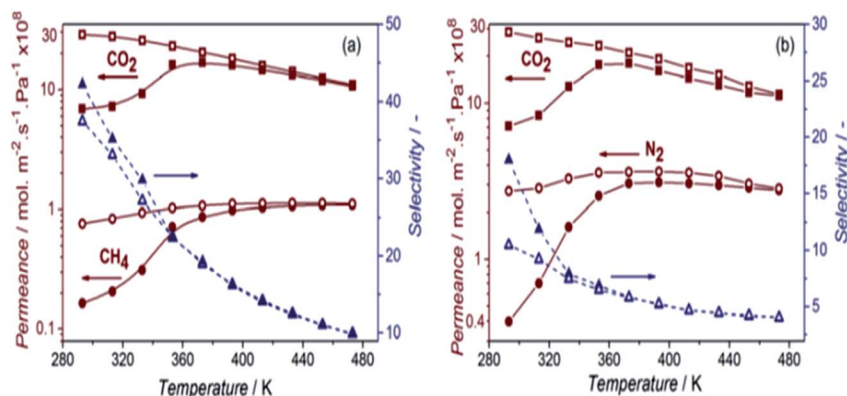
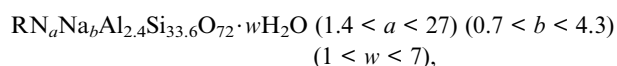


Fig. 8 Separation of equimolar mixtures of (a) CO<sub>2</sub>-CH<sub>4</sub> and (b) CO<sub>2</sub>-N<sub>2</sub> open symbols correspond to dry conditions, closed symbols to humid conditions, *i.e.* in the presence of 2.2 kPa of water; conditions: 0.6 MPa feed pressure, atmospheric pressure on permeate side, total feed gas flow rate 200 ml min<sup>-1</sup>, 200 ml min<sup>-1</sup> of sweep gas He. Reproduced from ref. 57 with permission from the Royal Society of Chemistry.

vapour more than that of methane. Ideal selectivities increased from 14 to 18 for temperatures of 303 and 343 K, respectively. A mass transfer model was developed based on Maxwell-Stefan approach for the prediction of vapour transfer through zeolitic pores of the membranes. Unilan isotherm was utilized for description of adsorption behavior of water vapour on NaA zeolite. The deviation of the model from experimental data was reasonable, while more satisfactory predictions are observed for temperatures higher than 333 K.

### SSZ-13

SSZ-13 (structure type CHA) is an aluminosilicalite zeolite mineral belonging to the ABC-6 family of zeolites. Its chemical formula is



where RN is *N,N,N*-1-trimethyladamantammonium. The material was patented by Chevron research Company in 1985,<sup>56</sup> and has a potential use as a solid catalyst for the methanol-to-olefins (MTO) process.

Kosinov *et al.*<sup>57</sup> fabricated high-silica (gel Si/Al = 100) SSZ-13 membranes by hydrothermal secondary growth on the surface of  $\alpha$ -alumina hollow fiber supports. The membranes were evaluated for their performance in the separation of CO<sub>2</sub> from equimolar mixtures with CH<sub>4</sub> or N<sub>2</sub>. They tried to compare the separation of gas mixtures in dry and humid conditions to determine the potential of the SSZ-13 membrane for separation

of CO<sub>2</sub> from wet gas mixtures. The feed gas mixture was humidified by adding 2.2 kPa of water. Fig. 8 shows the results for the separation of dry and humidified CO<sub>2</sub>-CH<sub>4</sub> and CO<sub>2</sub>-N<sub>2</sub> as a function of temperature. The presence of water affects the permeance of all the gases, which should be predominantly due to partial blockage of the zeolite pores. At 293 K the gas permeance is substantially lower under humid conditions compared to dry conditions (Table 3). Due to the decreasing water coverage, the permeance of all of the gases increases with increasing separation temperature. Already at 393 K, the permeance under humid conditions is close to the permeance under dry conditions.

To understand the effect of humidity Kosinov *et al.* also studied adsorption of water on SSZ-13 crystals. The results of adsorption are shown in Fig. 10. From Fig. 9 it seems that the amount of adsorbed water decreases from 3.1 mmol g<sup>-1</sup> at 298 K to 0.32 mmol g<sup>-1</sup> at 393 K. At 473 K the adsorbed amount of water was below the detection limit ( $\sim 0.02$  mmol g<sup>-1</sup>). These results suggested that water partially blocks permeation of gases by adsorption into zeolite pores at low temperature. The hydrophobicity of high-silica SSZ-13 ensures nearly complete elimination of water adsorption at modest temperatures (473 K). It was concluded by Kosinov *et al.* that water will adsorb on and block some of non zeolitic pores at low temperature and, accordingly, improve the overall selectivity.

Due to their hydrophobicity, water in the feed mixture has only a small influence on the permeance at temperatures above 393 K. Hunger *et al.*<sup>58</sup> ensured that the hydrophobicity of high-silica SSZ-13 would eliminate water adsorption almost

Table 3 Permeance of gases at dry and humid conditions in separations of corresponding mixtures<sup>57</sup>

Gas	Permeation (10 <sup>-7</sup> mol m <sup>-2</sup> s <sup>-1</sup> Pa <sup>-1</sup> )					
	293 K, dry	293 K, wet	% of dry	393 K, dry	393 K, wet	% of dry
CO <sub>2</sub> (N <sub>2</sub> )	2.886	0.71	25	1.9	1.6	84
N <sub>2</sub> (CO <sub>2</sub> )	0.27	0.04	15	0.36	0.31	86
CH <sub>4</sub> (CO <sub>2</sub> )	0.76	0.16	21	0.11	0.098	89

completely at modest temperatures (at around 473 K). Water improves the CO<sub>2</sub>-N<sub>2</sub> and CO<sub>2</sub>-CH<sub>4</sub> selectivity when the temperature is low, which is attributed to preferential blocking of the hydrophilic, non-zeolitic defect pores. The hydrothermal stability of the high-silica SSZ-13 membrane was evaluated by a long (220 h) CO<sub>2</sub>-N<sub>2</sub> separation test with a humidified (9.5 kPa H<sub>2</sub>O) feed mixture at 393 K and 0.6 MPa feed pressure. The permeance and selectivity were stable during this endurance test, undermining the promise of high silica SSZ-13 membranes for application in the separation of hot and humid gas mixtures.

Further Kosinov *et al.*<sup>57</sup> studied the permeation data of a bulky SF<sub>6</sub> molecule in dry and wet conditions. The results are collected in Fig. 10. In dry condition SF<sub>6</sub> permeance gradually decreases with increasing temperature, which is characteristic for Knudsen (pore size 10–100 nm) and Poiseuille (pore size > 50 nm) flows. The presence of water reduces the SF<sub>6</sub> permeation by ca., 50% at low temperature. Their work suggested that the high-silica SSZ-13 membranes are promising candidates for separation of different CO<sub>2</sub>-containing mixtures at elevated pressure and temperature and in the presence of water vapour due to the low polarity of SSZ-13. The separation mechanism is based on a combination of adsorption and diffusion selectivity.

### Zeolite NaA (zeolite 4A)

Zeolite 4A molecular sieve is a kind of alkali metal silicic acid salt and can absorb water and other molecules with a critical diameter less than 4 Å.<sup>59</sup> Its chemical formula is Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·9/2H<sub>2</sub>O and silica-alumina ratio is SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ≈ 2.

Okamoto *et al.*<sup>60</sup> prepared zeolite NaA membranes *via* hydrothermal synthesis with a short reaction time of 3 h at 373 K using a gel with the composition Al<sub>2</sub>O<sub>3</sub> : SiO<sub>2</sub> : Na<sub>2</sub>O : H<sub>2</sub>O = 1 : 2 : 2 : 120 (in moles) and porous α-alumina support tubes seeded with zeolite NaA crystals. It was reported that zeolite NaA membranes were highly permeable to water vapour. Gases (H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, SF<sub>6</sub>) were permeable only when the membranes were completely dry. The gas permeances of zeolite

NaA membranes varied rather significantly from sample to sample. The completely dried membranes displayed gas permeation behavior, which was attributed to Knudsen diffusion, indicating the presence of interstitial spaces between the zeolite crystal particles, or non zeolitic pores. However, membranes displayed excellent water permselective performance in pervaporation (PV) and vapour permeation (VP) toward water/organic liquid mixtures. A mechanism of PV and VP based on the capillary condensation of water in the zeolitic and nonzeolitic pores and the blocking of other molecules from entering the pores was proposed.

The permeation of H<sub>2</sub>O vapour, CO<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub> and their binary mixtures through a thin zeolite-4A membrane has been investigated in the temperature range between 30 and 100 °C by Zhu *et al.*<sup>61</sup> The zeolite-4A membrane was synthesized with pre-treatment of the supporting TiO<sub>2</sub> by UV-photons. The membrane exhibited a high permeance property and maintained a high selectivity for water. The permeance of the water vapour in the binary mixtures was almost the same as its unary permeance and only weakly temperature-dependent. The permeances of the gaseous components were strongly suppressed by water, resulting in high selectivities for water removal from these gases. The suppression effect was ascribed to the strong adsorption affinity of H<sub>2</sub>O inside the zeolite-4 Å pores, which blocked the permeation of the second gas component through the membrane.

### Zeolite – MMMs and MOF (ZIF)

Separation performances (selectivity, flux) of polymeric membranes are usually quite low. However, polymeric membranes can be produced in high quantities at low cost. Inorganic membranes (zeolites, amorphous oxides, carbon) have very good separation performance but they are too expensive. The positive properties of those membrane materials can be combined by embedding inorganic active components into a polymeric matrix creating a composite membrane called mixed matrix membrane (MMM). Compared to original

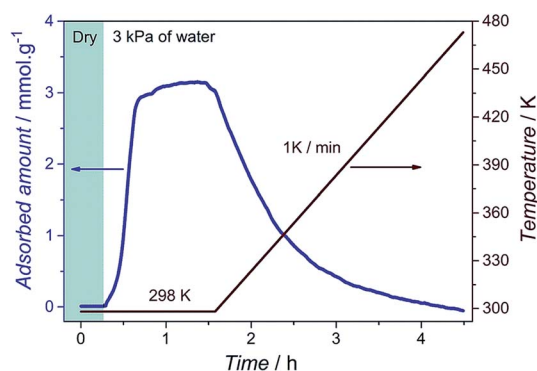


Fig. 9 Adsorption of water on SSZ-13 (Si/Al = 100) crystals measured N by TGA. During the experiment the sample was first completely dehydrated in dry He at 673 K, cooled down to 298 K and then subjected to a humidified (3 kPa H<sub>2</sub>O) He flow. After saturation the temperature was gradually increased to 473 K in the presence of the humidified He flow. Reproduced from ref. 57 with permission from the Royal Society of Chemistry.

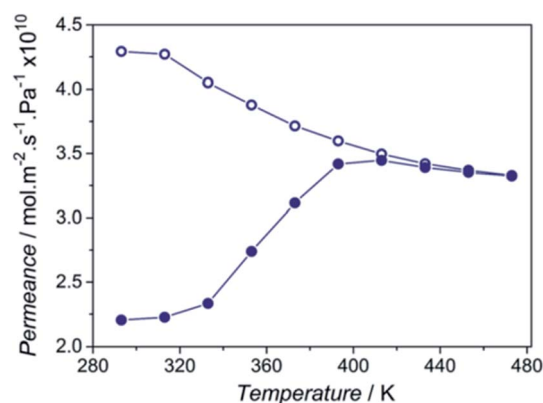


Fig. 10 Influence of water on SF<sub>6</sub> single gas permeance (open symbols – dry gas, closed symbols – 2.2 kPa of water; conditions: 0.6 MPa feed pressure, atmospheric pressure on permeate side, total flow rate 200 ml min<sup>-1</sup>, 200 ml min<sup>-1</sup> of sweep gas He). Reproduced from ref. 57 with permission from the Royal Society of Chemistry.

polymeric membranes, significant improvement in separation properties can be obtained.

The performance of the MMMs is influenced by several factors which are as follows;

- (i) Properties of polymer and fillers.
- (ii) Polymer filler compatibility.
- (iii) Process of membrane formation.

In the development of MMMs proper selection for polymer as continuous phase and inorganic filler as dispersed phase is important since they can affect membrane morphology and separation performance. MMMs have higher selectivity compared to continuous polymer matrix.

Most of MMMs with modified zeolite were engineered to reduce the interphase void and incompatibility. The most difficult task is to make MMMs defect free. Defects are formed generally due to incompatible interfaces between the polymer and the filler particle. A good adhesion between filler and polymer in MMMs is essential to avoid non-selective voids. Koros group<sup>62,63</sup> summarized some non-ideal factors which were always present in the interfaces and modified the Maxwell equation accordingly to illustrate their effects on the gas transport properties of MMMs. The use of MOFs as fillers in MMMs might result a breakthrough in the MMM field, since compatibility issues can eventually be overcome by optimizing the MOF linker-polymer interactions.<sup>64,65</sup> Li *et al.*<sup>66</sup> used silane coupling agent, (3-aminopropyl)-diethoxymethyl silane (APDEMS) to modify zeolite surface for mixed matrix membranes (MMM). Both permeability and selectivity of MMMs made from APDEMS modified zeolite are higher than those of MMMs made from unmodified zeolite at 20 wt% zeolite loading because of a decrease in the degree of partial pore blockage of zeolites.

Kim *et al.*<sup>67</sup> showed that the permeability of polysulfone nanocomposite membrane increased by introducing mesoporous materials whereas the selectivity did not change significantly and that was because of suitable compatibility between nanoparticles and polymer matrix. Ridzuana and Musab<sup>68</sup> showed the use of silane coupling agent is an excellent approach to increase the compatibility of the polymer and zeolite. It was concluded that surface modification of zeolite plays an important role to reduce the incompatibility of zeolite and polymer.

The use of MOFs as fillers in MMMs might result a breakthrough in the MMM field, since compatibility issues can eventually be overcome by optimizing the MOF linker-polymer interactions.<sup>64</sup>

Following are the different techniques suggested to eliminate the unselective gaps between the polymer and zeolite in the fabrication of MMMs<sup>69</sup>

- (1) Surface modification of the zeolite external surface.
- (2) Use of a silane coupling agent to introduce favorable interaction between polymer and zeolite.
- (3) Addition of a plasticizer to increase the flexibility of the polymer or chemically linking the two components together.
- (4) High temperature casting and removal of the dense films from the casting surface at a particular temperature.

MMMs which are comprised of inorganic materials distributed in polymeric phase are based on solid-solid system. When inorganic nanoparticles are added to the polymeric phase, it is predictable that resulting membrane separation properties become better than customary polymeric membranes due to the high gas permeance and selectivity of nanoparticles. Zeolites and many polymeric materials offer attractive transport properties for CO<sub>2</sub> separation. By mixing membrane materials, excellent membrane with high performance for CO<sub>2</sub> separation (selectivities of CO<sub>2</sub>/N<sub>2</sub> = 17.8–39.6) can be prepared.<sup>70–72</sup>

A variety of especially small pore zeolites have been used for their application in mixed matrix membranes (MMM). While early studies were focused on LTA zeolite, this hydrophilic zeolite turned out to be less attractive for gas separation from humid feeds because of the pore blocking by water.<sup>73</sup> Recent studies have focused, therefore, on more hydrophobic zeolites with a high molar SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio. Moore *et al.*<sup>73</sup> investigated the effect of humidified feeds on oxygen permeability of MMMs (zeolite + polymer). It was noted that MMMs composed of zeolite 4A that was dispersed in poly(vinyl acetate) were adversely affected by water adsorbed in the pores of zeolite 4A. Water adsorbed into the pores of hydrophilic molecular sieves can cause a decrease in the permeability of oxygen, and this will likely reduce the overall selectivity of MMMs prepared with such a sieve. As expected, the permeability reduction was more for the hydrophilic zeolite 4A than in the hydrophobic SSZ-13. Hydrophobic SSZ-13 MMMs were less affected by adsorbed water.

Metal-organic frameworks (MOFs) are hybrid organic-inorganic nanoporous materials that exhibit regular crystalline lattices with relatively well-defined pore structures. MOFs membranes can be constructed from metal ions or metal ion clusters and bridging organic linkers. It exhibits regular crystalline lattices with relatively well-defined pore structures and interesting properties. The porosity of MOFs is, in general, much higher than that of their inorganic counterpart, zeolites, justifying the designation 'framework'. MOFs (ZIF) can be fabricated in many different ways, making it possible to change their pore size and chemical properties.

ZIF-8 is highly attractive for gas separation applications and it is chemically stable in the presence of water and some aromatic hydrocarbons such as benzene, which are typical impurities in natural gas, making this particular ZIF composition potentially useful for the separation of CO<sub>2</sub> from CH<sub>4</sub>.<sup>74</sup> Yang and Chung<sup>75</sup> fabricated two types of advanced nanocomposite materials by incorporating as-synthesized wet-state zeoliticimidazolate frameworks-8 (ZIF-8) nano-particles into a polybenzimidazole (PBI) polymer. Mixed gas (CO<sub>2</sub>/H<sub>2</sub>) data show that the presence of water vapour impurity in the feed gas stream does not significantly influence the membrane performance at 230 °C. Thus, the newly developed H<sub>2</sub>-selective membranes may have bright prospects for hydrogen purification and CO<sub>2</sub> capture in realistic industrial applications such as syngas processing, integrated gasification combined cycle (IGCC) power plant and hydrogen recovery.

Mottillo and Friščić<sup>76</sup> first reported that in zeoliticimidazolate frameworks of Zn, Co and Cd, including ZIF-8, exhibited

sensitivity to CO<sub>2</sub> under mild conditions. The frameworks chemically reacted with CO<sub>2</sub> in the presence of moisture or liquid water to form carbonates, which was not reported previously. This phenomenon provides an explanation for conflicting reports on ZIF-8 stability to water and is of outstanding significance for evaluating the potential applications of metal–organic frameworks. This phenomenon may be applicable for other zeolite or zeolite membranes.

Nguyen *et al.*<sup>77</sup> studied the hydrophobic zeoliticimidazolate frameworks (ZIFs) with the chabazite (CHA) topology. All of these structures were hydrophobic as confirmed by water adsorption isotherms. All studied ZIFs were equally effective at the dynamic separation of CO<sub>2</sub> from N<sub>2</sub> under both dry and humid conditions without any loss of performance and can be regenerated simply by using a N<sub>2</sub> flow at ambient temperature.

Junaidi *et al.*<sup>78</sup> fabricated water-resistant MMMs by incorporating fluorocarbon functionalized SAPO-34 zeolite into polysulfone (PSf), to convert the hydrophilic SAPO-34 zeolite into hydrophobic SAPO-34 zeolite by using 1H,1H,2H,2H-Perfluorodecyltriethoxysilane (HFDS). PSf-10/HFDS 1.0 (10 wt% of modified SAPO-34 zeolite) MMM showed great enhancement in ideal gas separation (ideal selectivity CO<sub>2</sub>/CH<sub>4</sub> of 38.9 with CO<sub>2</sub> permeance of 278 GPU) compared to the neat PSf membrane and MMMs with unmodified SAPO-34 zeolite. On comparing the dry mixed-gas results, MMM incorporated with 10 wt% of unmodified SAPO-34 (PSf-10) suffered more than 90% reduction in separation performance during wet mixed-gas test. The actual selectivity of CO<sub>2</sub>/CH<sub>4</sub> for all MMMs was slightly lower than the corresponding ideal selectivity, either at dry or wet conditions. The gas separation performance of PSf-10/HFDS 1.0 MMM could be well sustained in both dry and wet gaseous system even after 24 h operation period. The only drawback of this membrane was the reduction in CO<sub>2</sub> permeance, about 7%, if comparing with humid single gas permeation. The presence of hydrophobic SAPO-34 in MMM established extra resistant towards water penetration, causing the dissolved CO<sub>2</sub> to exist as the retentate. Junaidi *et al.*<sup>78</sup> work suggested that the future work could be to study the potential of PSf-10/HFDS 1.0 MMM in the removal CO<sub>2</sub> and moisture simultaneously for downstream processing.

## Interpretation of experimental observations by a transport mechanism

Even though the presence of water in the feed stream displays different effects on the zeolite membrane performance as summarized in Table 4, some common patterns can be recognized among those effects. The factors that govern the effects are (1) hydrophilicity/hydrophobicity of the membrane (2) pore size and pore size distribution of the membrane (3) temperature and (4) partial vapour pressure of water in the feed stream.

Among many models proposed for the gas and vapour transport through the zeolite membrane, *e.g.* those based on surface diffusion<sup>55,69,81,82</sup> Stephan Maxwell and Knudsen approach,<sup>69,83</sup> Monte-Carlo and first-principles Car–Parrinello

molecular dynamics simulations,<sup>84</sup> the model proposed by Coronas and Santamaria<sup>8</sup> for the transport of ternary gas/vapour mixtures seems to be the most appropriate, in a slightly modified form, to explain the experimental observations, such as summarized in Table 4, in the presence of water vapour in the feed stream.

As shown in Fig. 11, the pores are classified into three groups according to the size, small (0.5–0.5 nm), intermediate (<2 nm) and large (2–5 nm). Let us now combine intermediate and large in one and call them large pores. The small pores may be considered as “intracrystalline pores” and large pores as “intercrystalline” pores, according to the designation by Nomura *et al.*<sup>85</sup> At present, these pores are assumed to be hydrophilic.

The gas mixture is composed of three components. Component A is a small polar molecule (*i.e.* water), that is preferentially adsorbed to the pore wall. Component B is a small, essentially non-adsorbing permanent gas and component C is a large size molecule that is also non-adsorbing and can only permeate the membrane through large pores. Then, the transport of component B and C will take place in the following way.

(1) At high temperature or low water vapour pressure, both small and large pores are open. Large pores do not contribute to selectivity. B over C selectivity is primarily due to the sieving (and diffusion) effect of small pores.

(2) When the temperature is lowered or water vapour pressure is increased the small pores are blocked while the large pores remain open. Permeation of B decreases considerably but that of C does not. As a result the selectivity of B over C decreases.

(3) As the temperature is further lowered or the water vapour pressure is further increased, adsorption of water vapour is significant and both small and large pores are blocked. As a result the permeation of both B and C decreases.

(3.1) If B is soluble in A, selectivity of B over C increases. Furthermore, when the solubility effect of B in A surpasses the pore blocking effect, permeation of B may even increase. When there is no water vapour in the feed stream or if the membrane is hydrophobic, all pores are open and the transport of B and C is the same as in case (1).

The observations summarized in Table 4 can then be explained as follows.

Case (1) will explain the observations made in ref. 75.

Case (2) will explain the observations made in ref. 34 and 47.

Case (3) will explain the observations made in ref. 35, 37, 41, 60, 73, 78 and 79.

Case (3.1) will explain the observations made in ref. 32, 36, 38 and 80.

The combination of cases (1) and (3.1) will explain the observations made in ref. 45.

The combination of cases (1) (2) and (3) will explain the observations made in ref. 15.

Although the above model does not involve detailed mechanisms of the molecular transport through the zeolite pores, the model is simple but sufficient to explain many experimental results.

Table 4 Separation of gases in presence of moisture/water

Membrane	Preparation	Feed	Temperature range	Results	Ref.
Porous silica	Sol-gel, method, coated on alumina tube	H <sub>2</sub> , He, CO <sub>2</sub> , N <sub>2</sub> + moisture	35 °C	In humid conditions CO <sub>2</sub> and N <sub>2</sub> permeances decreased drastically	79
FAU membrane	Hydrothermal seeded growth	CO <sub>2</sub> /H <sub>2</sub> , CO <sub>2</sub> /N <sub>2</sub> and CO <sub>2</sub> /CH <sub>4</sub>	60 °C	FAU membranes are CO <sub>2</sub> selective. Presence of water vapour enhances the CO <sub>2</sub> flux significantly	80
MFI	<i>In situ</i>	H <sub>2</sub> + 500 ppb H <sub>2</sub> O	303–673 K	At room temp ( <i>T</i> ). Permeation was low in comparison with dried H <sub>2</sub> permeation and then increased with increase in <i>T</i> and then leveled off around 100 °C	15
MFI (ZSM-5)	Hydrothermally on alumina tubes	CO <sub>2</sub> /N <sub>2</sub> + moisture	Room temperature –140 °C	A steady state reduction of the gas permeation of about 40% for a water concentration of 10 v/v% at 373 K. Promotes CO <sub>2</sub> /N <sub>2</sub> separation due to defective pore blockage and formation of (bi)carbonate stable intermediates	33
MFI (ZSM-5, (Si/Al ~ 80) and aluminium -free silicalite)	Dip coating on alpha alumina	H <sub>2</sub> /CO <sub>2</sub> , H <sub>2</sub> /CO <sub>2</sub> /H <sub>2</sub> O	300–350 °C	Water vapour lowers H <sub>2</sub> and CO <sub>2</sub> permeation to the same extent, resulting in negligible effect on the H <sub>2</sub> /CO <sub>2</sub> separation factor. The suppression effects of water vapour on H <sub>2</sub> and CO <sub>2</sub> permeation increase as temperature decreases and water vapour pressure increases. Water confined in MFI zeolite pores has the same suppression effect on the permeation of H <sub>2</sub> and CO <sub>2</sub> through the MFI zeolite membrane as observed on silicalite membrane	38
MFI (different type ZSM-5)	Gel method on alumina and stainless steel support	CO <sub>2</sub> /N <sub>2</sub> bubbled through water	300–475 K	The CO <sub>2</sub> permeation fluxes decreased about 54% and 29% for a feed pressure of 1.7 and 2.2 bar, respectively, without use of a sweep gas in the permeate stream, with the separation factor remaining essentially unchanged	36
ZSM-5				Although the pure N <sub>2</sub> and SF <sub>6</sub> permeances decreased after humidification of the feed stream (61% for N <sub>2</sub> and 16% for SF <sub>6</sub> ), the initial values were recovered after water removal	35
MFI (three different counter ions) and silicalite	Hydrothermally (alumina disc.)	CO <sub>2</sub> /H <sub>2</sub> bubbled through water	Room temp. –150 °C	Counter ions had a significant effect. For the H <sub>2</sub> /H <sub>2</sub> O system, H <sub>2</sub> permeation is 5–6 times lower than pure H <sub>2</sub> . For the CO <sub>2</sub> /H <sub>2</sub> O system CO <sub>2</sub> permeation decreases to a minor extent. For the H <sub>2</sub> /CO <sub>2</sub> /H <sub>2</sub> O system permeation of both gases decrease	39
ZSM-5			Room temperature		37

Table 4 (Contd.)

Membrane	Preparation	Feed	Temperature range	Results	Ref.
	Hydrothermally on $\alpha$ -alumina (4 types)	Moisture saturated $\text{CO}_2/\text{N}_2$		An increase of the membrane selectivity in the separation of a moisture-saturated equimolar $\text{CO}_2/\text{N}_2$ mixture by a surface-modified ZSM-5 membrane. At room-temperature $\text{CO}_2/\text{N}_2$ separation factor was about 50 for dry mixture and about 60 for wet mixture steady-state separation. It was believed that water blocked partially both the MFI adsorption sites and the intercrystalline non-zeolite pores, overcoming $\text{N}_2$ permeation and thus increasing the $\text{CO}_2/\text{N}_2$ separation factor	61
NaA	Hydrothermally on $\alpha$ alumina	Different gases	Room temp.	Impermeable to every gas unless dried completely, Knudsen diffusion	55
NaA	Hydrothermally	$\text{CH}_4$ and $\text{H}_2\text{O}$ vapour	303–342 K	Ideal selectivity of water vapour was more than methane. A mass transfer model was developed. Based on Maxwell–Stefan approach	53
Defect free FAU-type (Y)	Hydrothermally on $\alpha$ alumina	$\text{CO}_2/\text{N}_2$ dried and moist	23–200 °C	Decreased the P of $\text{CO}_2$ and $\text{N}_2$ , $\text{H}_2\text{O}$ vapour enhanced the $\text{CO}_2$ selectivity at 110–200 °C, but drastically lowered below 80 °C. At 200 °C with increasing $\text{H}_2\text{O}$ permeation. $\text{CO}_2$ selectivity increased and then decrease with increasing water partial pressure. $\text{N}_2$ permeation through large intercrystal pores	42
SAPO-34	Hydrothermal synthesis	$\text{CO}_2/\text{CH}_4$	Room temperature	Humidity has strong effect on permeation of gases and the effect depends on non-SAPO pores. Water almost blocks the SAPO pores in high quality membranes. Low quality membranes have larger pores and thus permeation through these pores increases with humidity. The $\text{CO}_2$ recovered the original permeances and selectivity after calcination at 573 K for 24 h. Water had a strong effect on gas permeation through SAPO-34 membranes: water almost completely blocked the SAPO pores	45
DDR type zeolite	Hydro thermally zeolite crystal on alumina	$\text{CO}_2/\text{CH}_4$	280–373 K	Permeation of $\text{CO}_2$ decreased in the wet gas feed at 280 K, separation factor increased. At 373 K no changes were observed between dry and wet feed in separation factor and permeation	

Table 4 (Contd.)

Membrane	Preparation	Feed	Temperature range	Results	Ref.
DDR type zeolite	Hydrothermally on porous alumina tube	CO <sub>2</sub> /CH <sub>4</sub>	298 K	While the permeance of CH <sub>4</sub> was not affected by water vapour, the presence of 3% water in the gas stream reduced the CO <sub>2</sub> permeance to half of that for a dry feed stream, resulting in a 50% reduction in the CO <sub>2</sub> /CH <sub>4</sub> selectivity	48
MMMs (fluorocarbon + SAPO-34)	Dry-wet phase inversion	CO <sub>2</sub> /CH <sub>4</sub> bubbled through water	30 °C	Huge reduction in gas separation performance due to the blockage of SAPO-34 pores	78
<b>MMMs membranes</b> Zeolite 4A/acetate and SSZ-13/PVAC	Mixing the components in dichloro-methane and dried	Humidified O <sub>2</sub>	35 °C	Water can affect both the polymer and sieve phases. Decrease in permeability of O <sub>2</sub>	73
ZIF-8/PBI	Two types. By mixing both components in solvent and dried	Humidified CO <sub>2</sub> /H <sub>2</sub>	230 °C	Impurities such as H <sub>2</sub> O vapour existing in the model syngas have no significant impact on the H <sub>2</sub> /CO <sub>2</sub> separation	75

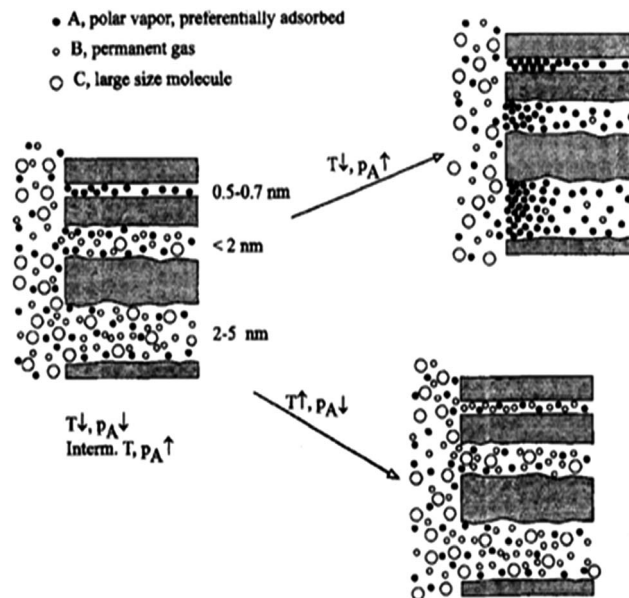


Fig. 11 Influence of temperature and partial pressure on the selectivity of a zeolite film. Reproduced from ref. 8 with permission from the Taylor & Francis.

## Effect of grafting a functional group on zeolite

Grafting a functional group on zeolite can change water absorption in zeolite. Zeolite's chemical composition can be tuned by introducing other heteroatoms (Ti, Sn, Fe, Cu, Co *etc.*), both in framework or extra-framework positions, and consequently, the nature of the zeolite active sites will change (acid-base or redox centers). Those "tailor-made" physicochemical abilities, together with their high hydrothermal stability and "non toxic" character, have allowed their wide application in industry.<sup>86</sup>

Amine-containing adsorbents are often tolerant to the occurrence of moisture in the feed.<sup>87</sup> Because of the very nature of the amine-CO<sub>2</sub> interactions, the CO<sub>2</sub> uptake is actually enhanced by the presence of moisture. Under dry adsorption conditions, surface amine groups interact with CO<sub>2</sub> to form carbamate with a stoichiometric CO<sub>2</sub>/N ratio of 0.5, whereas under proper humidity conditions, bicarbonate with a stoichiometric ratio CO<sub>2</sub>/N = 1 may be formed. In contrast, in the presence of other adsorbents such as zeolites, CO<sub>2</sub> adsorption is severely inhibited by moisture because of unfavorable competition.<sup>88</sup>

On introducing the amine functional group in Y-type zeolite the adsorption of CO<sub>2</sub> in zeolite is enhanced.<sup>89</sup> Sanaepur *et al.*<sup>90</sup> used 3-aminopropyl(diethoxy)methylsilane (APDEMS) for silylation of a NaY zeolite surface to investigate the effect of surface modified zeolite (NaY-sm) in cellulose acetate (CA) gas separation membranes. Better gas permeation results were obtained using NaY-sm instead of NaY in the membranes.

Faria *et al.*<sup>91</sup> demonstrated that a combination of Lewis and Brønsted acid sites, together with a metal function on

a hydrophobic support, exhibits improved hydrothermal stability and resistance to leaching of the active sites. Conventional NaX faujasite zeolites, in which the sodium ions act as weak Lewis acid sites for the keto-aldose isomerization of glucose, are rapidly deactivated in liquid water at 383 K. In contrast, functionalized MWCNT-NaX zeolite keeps its crystalline structure in this harsh environment.

Jadhav *et al.*<sup>92</sup> impregnated monoethanol amine (MEA) on zeolite 13X and examined the hybrid material for CO<sub>2</sub> adsorption at different temperatures. The MEA-impregnated adsorbent showed higher CO<sub>2</sub> capture capacity than zeolite 13X at 120 °C, and exhibited improved CO<sub>2</sub> selectivity, which was enhanced further in the presence of moisture.

Taib *et al.*<sup>93</sup> demonstrated that grafting the functionalized group on the surface of adsorbents (such as zeolite) did not modify the original structure but altered their original hydrophilic nature to hydrophobic.

Jin *et al.*<sup>94</sup> modified an asymmetric silica membrane supported on a porous alumina tube substrate with hexamethyldisilazane (HMDS) *via* dip-coating. The membrane was used for the separation of ethanol/water mixture by pervaporation. The surface of the silica membrane chemically bonded with trimethylsilyl groups (-Si(CH<sub>3</sub>)<sub>3</sub>) of HMDS showed hydrophobicity.

## Summary

Zeolite membranes are thermally stable with good chemical resistance and mechanical strength in comparison to pure polymer membranes but they are very fragile and brittle. Furthermore, the technology for fabricating commercial zeolite membranes is still in the developmental stage while the technology for commercial production of polymeric membranes is very mature with applications in a series of industrial processes.

A common problem in zeolite membrane synthesis is that, despite the use of a pre-defined methodology, it is difficult to obtain membranes with consistent and predictable properties. In the past decade not much research has been done on the moisture effect on the gas separation *via* zeolite membranes, since zeolite membranes are relatively new in comparison to polymeric membranes. However, it is known that there is moisture effect on the gas separation for a number of zeolite membranes such as SAPO-34, MFI and DDR. The property of zeolite membranes (performances *etc.*) depends on the synthesis methods and it could also be possible that the effect of moisture/water is different for different zeolite membranes. Despite many unknown factors one thing is certain that hydrophobicity or hydrophilicity of zeolite, which is tunable by grafting, introduction of heteroatoms and changing Al/Si ratio, temperature and water vapour pressure of the feed gas stream play significant roles on the effect of water on zeolite membrane separation of gases. The mechanism for the CO<sub>2</sub> separation from other mixed gases in presence of moisture is very complicated. More study on this subject is necessary as zeolite membranes seem to become very important in future for the chemical, petroleum, gas processing industries.

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