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Preliminary study on the feasibility of using a zeolite A membrane in a membrane reactor for methanol production

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HIGHLIGHTS

- Permeation of CO2,H2,H2O mixtures through a zeolite A membrane was studied
- Effects of temperature, partial pressures, total pressure were examined
- Experimental results provide insight towards the development of a membrane reactor
- Good water selectivity, with low H2 and CO2 flux was seen in many cases
- Surprising high water partial pressure in permeate, caused by a temperature gradient

Abstract

The permeation of a mixture containing H_2, CO_2 and water through a zeolite membrane was studied under several operating conditions. The aim was to obtain insight on the feasibility of using such membrane in a zeolite membrane reactor for CO_2 hydrogenation to methanol. The effects of total pressure (100-270 kPa), water partial pressure (10-18 kPa) and temperature (160-260ºC) were studied. Promising water-permanent gas separation factors were obtained up to 240ºC. A surprisingly high water partial pressure was found in the permeate in some cases, which is explained by the radial temperature gradient in the experimental system. The good capability of this zeolite A membrane to selectively separate water vapor makes it a promising material for its use in a zeolite membrane reactor.

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Graphical abstract
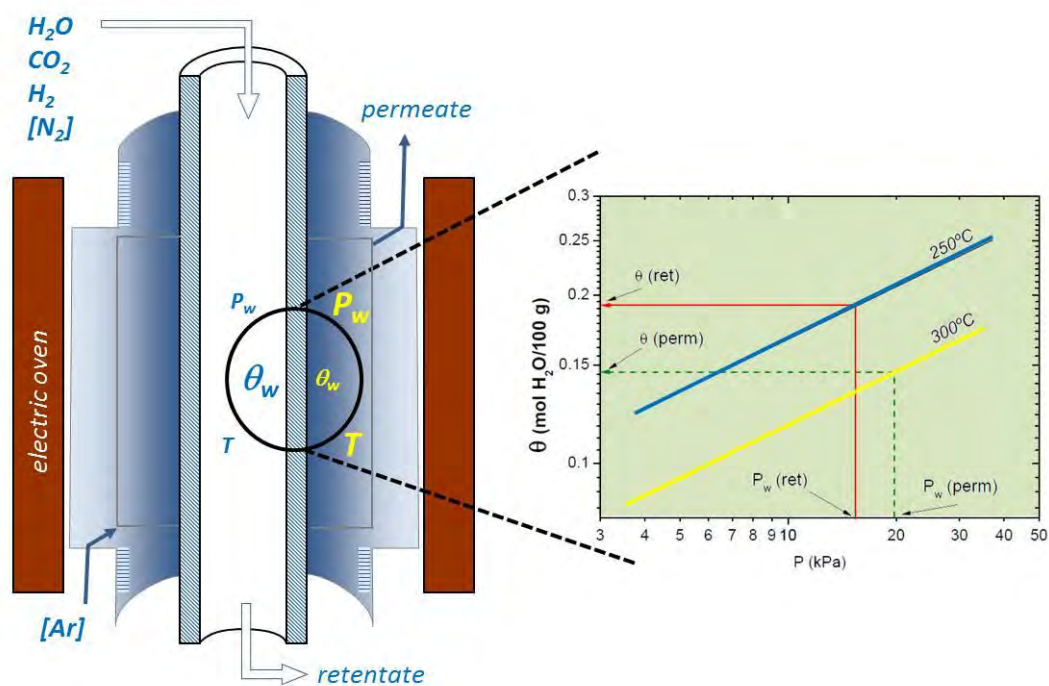
1. Introduction

Membrane reactors are a key tool for process intensification because they allow integrating a catalytic reaction and the separation of products in a single unit [1][2]. In addition, higher conversion and lower reaction temperature can be reached by applying membrane reactors. Among the different kinds of membrane available for their use in membrane reactors, zeolite membranes provide quite special properties: a) good chemical and physical stability, b) possibility to tailor the pore size and c) feasibility of changing the chemical composition of the zeolite, thus selecting the desired interaction of the zeolite surface with the chemical compounds. An example of the last point is the variation from hydrophilic zeolites (like zeolite A) to hydrophobic (e.g. silicalite) by varying the Si/Al ratio in the framework. Zeolite membranes have attracted the interest of many groups since they were first described [3] and even more since they were applied industrially [4]. The interested reader can find several reviews on zeolite membranes and their application in membrane reactors [5][6][7][8][9][10] [11][12][13][14]. Under certain conditions, water or other compounds formed via reaction condense or adsorb in the pores of the zeolite, preventing other compounds permeating through the membrane. Application of zeolite membranes in a membrane reactor by removing water from a reaction media containing permanent gases has been examined with Fischer-Tropsch synthesis of hydrocarbons [15][16], in the synthesis of methanol or dimethyl-ether (DME) from synthesis gas (i.e. a mixture of CO, CO_2 and H_2)[17,18] and in other chemical productions.

Methanol is one of the most important basic chemicals, with a large production worldwide and could be the intermediate step in several Gas-to-Liquids technologies, such as methanol-to-olefins (MTO), or methanol-to-gasoline (MTG). By considering the reactions for methanol synthesis

$$CO + 2\,H_2 \Leftrightarrow CH_3OH \qquad\qquad (1)$$

$$CO_2 + 3\,H_2 \Leftrightarrow CH_3OH + H_2O \qquad\qquad (2)$$
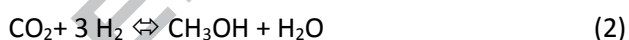
it is quite obvious that removing the methanol or the water formed in the reaction, the achievable conversion can be increased (*Le Chatelier*'s principle). Equilibrium conversion is low at low pressures, for example at 0.5 MPa and 220ºC the methanol yield for CO_2 hydrogenation would be lower than 1%. This explains why methanol synthesis is industrially carried at high pressure (5-10 MPa) as a way to achieve higher conversion, and even so the typical conversion per pass is often quite low (10-15%). Therefore, if the conversion can be increased by removing the reaction products would be advantageous, both because it would allow lower operation pressures and because it would provide a lower flowrate in the recirculation loop. The use of a membrane reactor was firstly tested experimentally by Struis et al. [19][20], using a Nafion membrane. Although they were able to increase the conversion beyond that achievable with a conventional reactor, the maximum operating temperature allowed by Nafion was 200ºC. This temperature is significantly lower than the mean reaction temperature in industrial methanol synthesis (c.a. 250ºC) and therefore the spatial time was too high. The use of a zeolite membrane reactor was suggested by Menéndez et al. [21] and Gomez et al. [22] shown experimentally that it was possible to selectively remove water and methanol from

a mixture of gases using a zeolite membrane. Piera et al. [23] showed the separation of alcohols from permanent gases. Sawamura et al. [24] showed the separation of steam from gas mixtures using a mordenite membrane. Gallucci et al. [25] proven experimentally that it was possible to achieve a higher conversion during methanol synthesis using a zeolite membrane reactor than with the traditional reactor, and the possibilities of such a reactor have studied by means of a mathematical model [26]. However, the former researchers recognized that there was a lack of experimental results describing the variation of separation factor with the operating conditions in a zeolite membrane.

Another potential application of a membrane reactor is dimethyl ether (DME) production. DME is a promising fuel, which can be employed both in explosion and compression (Diesel) engines. Although DME can be obtained from methanol, it is advantageous to obtain it directly from synthesis gas. By converting methanol to DME in the reactor, the achievable conversion is increased.

The synthesis of dimethyl-ether (DME) from syngas, described by

$$2\ CO + 4\ H_2 \Leftrightarrow CH_3OCH_3 + H_2O \qquad\qquad (3)$$

$$2\ CO_2 + 6\ H_2 \Leftrightarrow CH_3OCH_3 + 3H_2O \qquad\qquad (4)$$
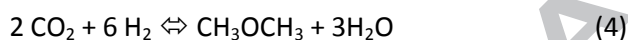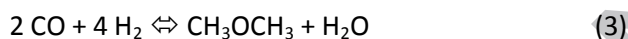
is another case of equilibrium-limited reaction, where the removal of water from the reaction environment can provide an increase in conversion with respect to the conventional reactor. Diban et al. [17,18] suggested from a mathematical model that a membrane reactor with a membrane with suitable water-permanent gas separation factors could provide significant advantages. The mathematical model assumed water/permanent gases separation factor based on previous results, but it is obvious that a clear relationship between selectivity and operating conditions for this kind of separations has not been achieved.

The objective of this work is to experimentally study the separation of water-permanent gas mixtures under conditions that can be relevant for methanol or DME, e.g. methanol synthesis from CO_2 and H_2.

2. Experimental system
2.1. Zeolite membrane synthesis

Zeolite A membranes were prepared on the outer surface of porous α-alumina tubes (NikkatoCo, o.d. 12 mm, i.d. 9 mm, length 100 mm, pore size 1.25 μ m) by a secondary growth method. Supports were immersed in a synthesis mixture having molar ratio of 1 SiO_2 : 0.5 Al_2O_3 : 1 NaO : 75H_2O=1:0.5:1:75 after applying seed crystals, heated at 100 ºC for 4 hours. XRD and SEM analyses showed a formation of zeolite A membrane on the support. The zeolite membrane was tested in the pervaporation of a mixture water-methanol, yielding a separation factor over 10000. Nitrogen permeation for this membrane was $1.54\cdot10^{-9}$ mol.m^{-2}.s^{-1}.Pa^{-1} at a mean pressure of 0.2 MPa and room temperature and rose to $3.38\cdot10^{-9}$ mol.m^{-2}.s^{-1}.Pa^{-1} at the same pressure and 160ºC. This large increase in permeation corresponds to what is named as activated diffusion, and is a characteristic of flow in very small pores.

2.2 Permeation tests

Figure 1 shows a schematic diagram of the experimental setup. Gas feeds were delivered by mass flowmeters (Brooks). Water with a regulated flow rate by an HPLC pump was fed to a stainless steel tube, that was submerged in a sand bath, with a nitrogen stream to achieve a smoother flow. The mixture of water and gas (after adding CO_2 and H_2) was fed to the inner part of a zeolite membrane sealed in a stainless steel module. Ar was fed to the external side of the membrane as sweep gas. The stainless steel module with the zeolite membrane was located in an electrical furnace, whose temperature was controlled by a thermocouple inserted in the center of the membrane tube. Viton o-rings were used below 180ºC to seal the membrane to the module, while gaskets made with a mixture of silicone grease and graphite powder were used at higher temperature. Two valves at the exit of permeate and retentate allowed controlling the pressure at both sides of the membrane. Both permeate and retentate streams were cooled in an ice-salt bath and the condensed product was weighted. The resulting gases were analyzed by gas chromatography and their flow was measured with a bubble meter.

The separation factor, according to the IUPAC rules [27], is defined from the ratio of concentrations of two compounds in permeate and retentate.

$$SF_{ij} = \frac{[p_i/p_j]_{perm}}{[p_i/p_j]_{retent}} \qquad (5)$$

Repeated experiments showed an experimental error in separation factor around 5%.

Figure 1. Scheme of the experimental system. The membrane module is located inside the oven.
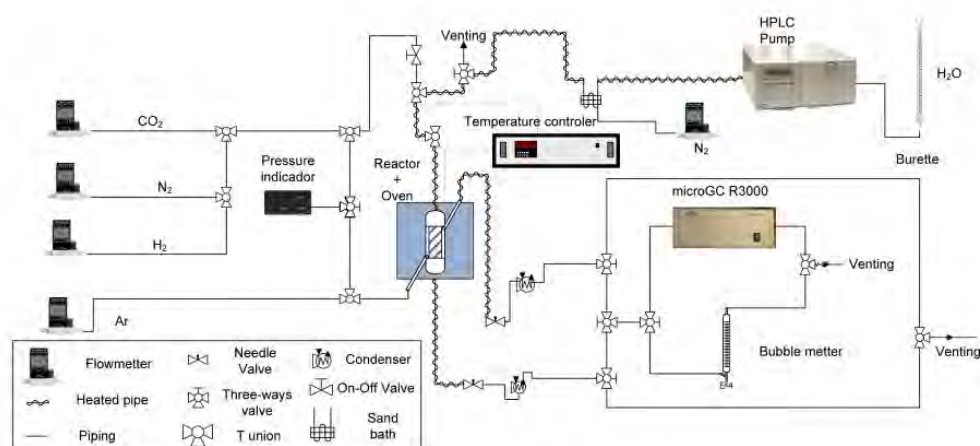
3. Experimental results

3.1. Effect of temperature and partial pressure of water

A series of experiments were performed by varying the temperature between 160 and 260ºC and the partial pressure of water between 10 and 18 kPa. These values of partial pressure of water would be similar to those obtained in the hydrogenation of CO_2 at 220ºC and 0.5 MPa. Other experimental conditions are given in Table 1.

Table 1. Flow rates in the feed to the permeate side (sweep gas) and the feed side, in gas-water vapor separation experiments.

	Permeate side	Feed side			
	Ar	**N$_2$**	**CO$_2$**	**H$_2$**	**H$_2$O**
Flow rate cm^3 (STP).min^{-1}	10	55	50	120	25-50

Figure 2 reports the variation of water flux as a function of temperature. Results obtained with three different water partial pressures in the feed are shown. Water flux increased with the partial pressure of water in the feed, which is quite in accordance with expectations. The variation of water flux with temperature follows the trend already observed in the permeation of other compounds that can be adsorbed [28]: a) at low temperature the flux increased with temperature up to a maximum, b) after the maximum the flux decreased with temperature, and c) eventually the flux increased again with temperature. The first two parts agree with a mechanism of diffusion of adsorbed molecules, in which the permeation depends on two factors: diffusivity and concentration of adsorbed molecule. At low temperature the rise of temperature increases diffusivity of the adsorbed molecule, and thus resulted in the flux increase. After the maximum, the decrease in concentration of adsorbed molecules becomes so large that the product of both factors decreases. Finally, when the temperature is large enough the flux is mainly in gas phase (activated flow) and rises again with temperature.
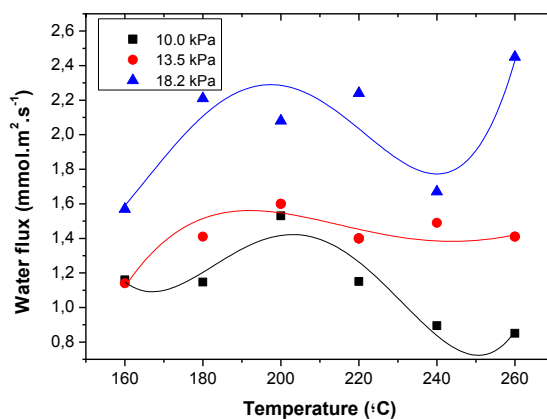
Figure 2. Effect of temperature and water partial pressure in the feed on the water flux through the membrane. Parameter: partial pressure of water in the feed. Lines are only for eye aid.

The effect of the operating conditions (temperature and partial pressure of water in the feed) on the separation factor (water/H_2 and water/CO_2) is shown in Figure 3. As a reference, the simulations of a membrane reactor in [21] employed a SF (CH_3OH/H_2) of 20. As temperature increases, a maximum in separation factor is achieved. At temperatures over 240ºC, the separation factor becomes too low, probably around the limit to be useful in a membrane reactor. The decrease of separation around this temperature agrees with the experimental results by Gallucci et al. [25] who found that above 240ºC the membrane reactor was not able to outperform the traditional reactor. The effect of water partial pressure on the separation factors is small in the range of operating conditions studied in this work, compared with the effect of temperature.
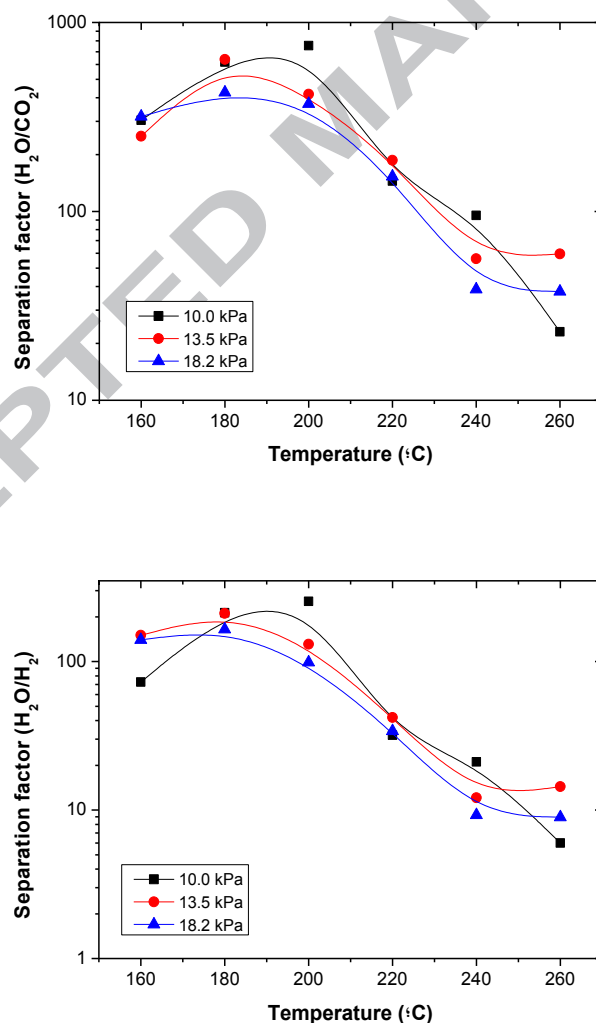

Figure 3. Effect of temperature on the separation factor. Total pressure at both sides 101 kPa. Top: SF (H_2O/CO_2), bottom: SF (H_2O/H_2). Lines are drawn as eye aid.

3.2. Effect of pressure drop through the membrane

In this section two experiments are compared: a first one in which the total pressure at both sides of the membrane was the same (101 kPa) and a second experiment in which the pressure of the feed was higher (240 kPa) than in the permeate side (101 kPa). The separation factor is shown in Figure 4. The negative effect of a different total pressure is quite evident, which is clearly explained by the existence of some defects, in which a non-selective flow appears when the pressure at both sides is different. These defects are probably inter-crystalline pores. The flow through these defects is very low when the total pressure is the same at both sides, but is evidenced by the increase in flux of permanent gases in the presence of a total pressure gradient. As an example, in the experiment shown in Figure 4, the hydrogen flux increased by a factor of 3.5. From the point of view of the application of this kind of membranes in a membrane reactor, this result would limit the operation to a situation where the pressure at both sides was the same, using some kind of sweep gas in the permeate side.
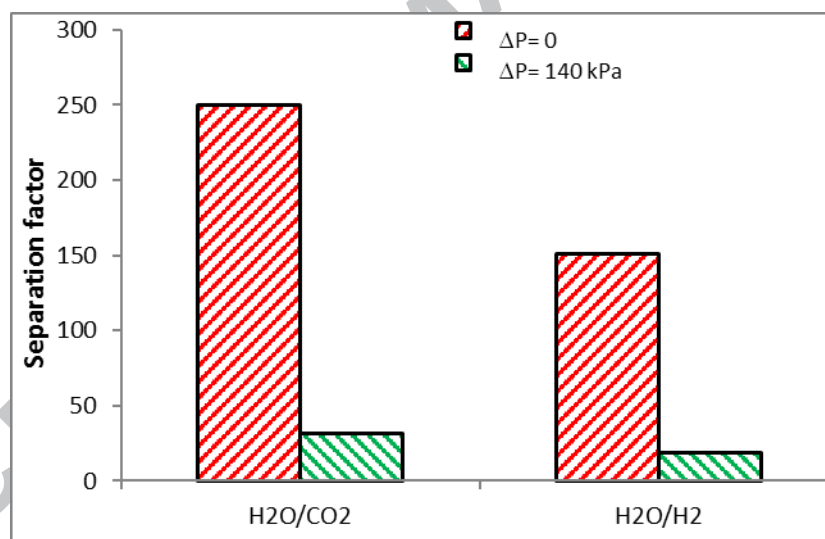

Figure 4. Comparison of the separation factor with the same or a different pressure at both sides of the membrane. T= 160ºC. Water molar fraction in the feed= 0.18.

3.3. Influence of total pressure

If the operation pressure was increased, but keeping the same pressure at both sides of the membrane, an increase in water flow was observed (Figure 5), but with some decrease in the separation factor (Figure 6). The flow increase can be explained by the higher driving force (i.e. difference in partial pressure at both sides of the membrane). The decrease in separation factor suggests that the increase in the flow of permanent gases is larger than the increase in the flow of water. This can be explained because the driving force for water permeation is not increasing according to the large water partial pressure in the feed, at least in these experimental conditions. As we will show later, the water partial pressure in the permeate

achieved a quite large value under some of the operating conditions employed in this work, which limits the water permeation.
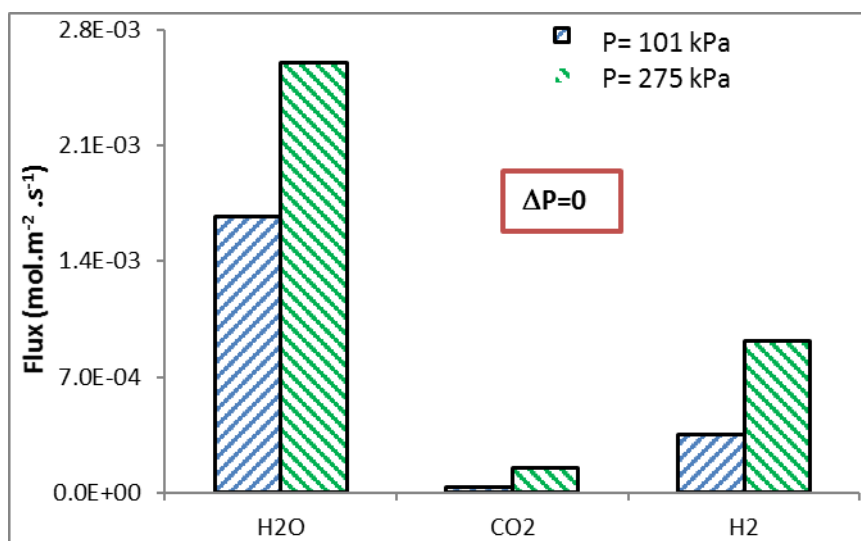

Figure 5. Effect of total pressure on water flow. T= 240ºC. Molar fraction of water in the feed=0.18.
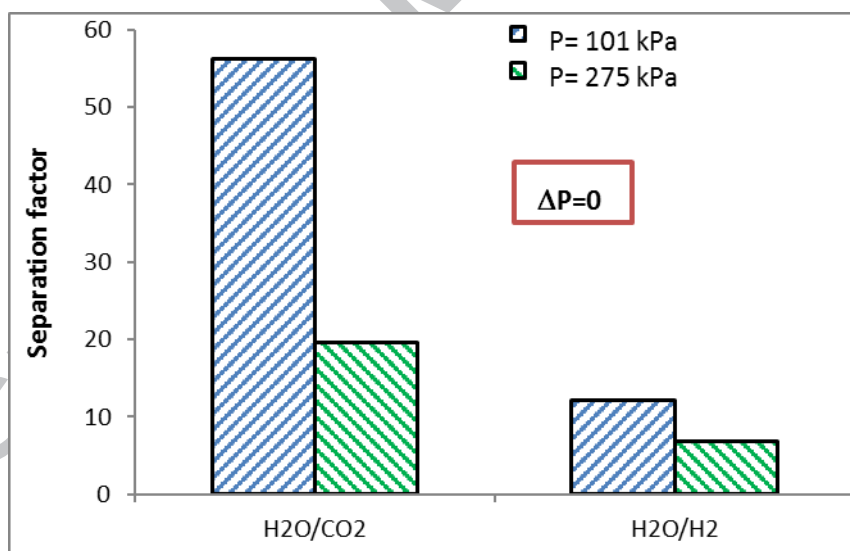

Figure 6. Effect of total pressure on the separation factors. T= 240ºC. Water molar fraction in the feed=0.18.

3.4. On the surprisingly high water partial pressure in permeate

By comparing the water partial pressure in permeate and in retentate (Table 2), a surprising result was seen in these experiments: It was higher in the permeate than in the retentate. This result is opposed to the general assumption that a gas is transported from the side where it is at higher concentration (or partial pressure) towards the side where it is at lower concentration (or partial pressure). An explanation to this surprising behavior can be

given by considering that the driving force for water permeation is not the gradient of water partial pressure in the gas phase, but the gradient of adsorbed water concentration in the membrane. This consideration, together with the difference in temperature at both sides of the membrane (resulting from the fact that the membrane module is heated by an external furnace), explains this counterintuitive result. The experimental temperature difference between the internal and the external side was measured, and it was c.a. 30ºC. As shown in Figure 7, the variation in adsorbed water concentration in a zeolite with such a difference of temperature can be quite large. It is possible that the adsorbed concentration of water in the permeate side (green-dotted line) was lower than in the retentate (red-solid line), although the water partial pressure followed the opposite order.

Table 2. Partial pressure of water in permeate and in retentate

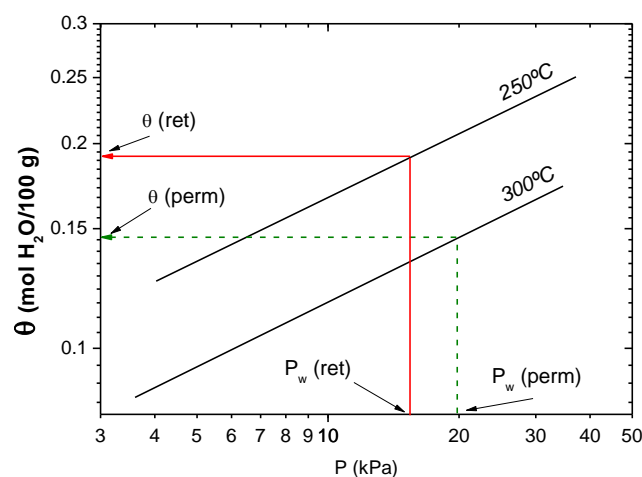| T in retentate side (ºC)	P H$_2$O feed (kPa)	P H$_2$O retentate (kPa)	P H$_2$O permeate (kPa)
160	18	18	24
160	13	13	18
160	10	9	18
180	18	18	29
180	13	13	21
180	10	9	21
200	10	10	22
200	18	18	28
200	13	13	23
220	18	18	29
220	13	12	21
220	10	9	17
240	10	9	14
240	18	17	23
240	13	13	21
260	18	17	30
260	13	13	20
260	10	10	13

Figure 7. Illustration of the effect of different temperatures in permeate and retentate sides. Adsorption equilibrium data taken from [29]

4. Conclusions

The effect of temperature and water partial pressure on the water flux and the $SF(H_2O/CO_2)$ and $SF (H_2O/H_2)$ has been measured. These results provide the foundation for a better design of a membrane reactor for CO_2 hydrogenation to methanol. Good separation factors were obtained, although a decrease was observed when the temperature was raised over 240ºC.

In a practical operation, the blocking of pores for the transport of hydrogen or carbon dioxide requires a minimum partial pressure of water. It could be possible to add some water to the feed, but this would decrease the yield at the equilibrium. A better alternative, to be explored in future work, is to have in first place a conventional reactor and in second place a membrane reactor. This would provide enough water content in the feed to the zeolite membrane reactor.

The use of the same pressure at both sides of the membrane, and thus the use of a sweep gas, is needed to keep good separation factors.

As surprising result was that under the employed operating conditions the water partial pressure in permeate was higher than in retentate. This was explained by a temperature gradient in the experimental system, in such a way that the temperature in the permeate side was higher than in the retentate side. This result suggests that water flux can be improved by applying a temperature gradient, with higher temperature at the permeate side.

Acknowledgement

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