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Catalysis Today, Volume 364, 15 March 2021, Pages 270-275

DOI: 10.1016/j.cattod.2020.03.014

Zeolite membranes: Comparison in the separation of $H_2O/H_2/CO_2$ mixtures and test of a reactor for CO_2 hydrogenation to methanol

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Abstract

A zeolite membrane reactor can be employed for hydrogenation of CO_2 to methanol. The removal of water from the reaction environment would increase the reaction rate and the achievable conversion. The separation of water from mixtures containing CO_2, hydrogen and water at suitable temperatures for this reaction was tested with several zeolite membranes (zeolite A, mordenite, zeolite T, chabazite and Ti-Chabazite). Zeolite A provided the best H_2O/H_2 separation factor. Preliminary experiments comparing a traditional reactor and the combination of a traditional reactor with a membrane reactor show that the yield of methanol was improved, in one case being higher than the limit corresponding to the thermodynamic equilibrium in a conventional reactor.

1. Introduction

Hydrogenation of CO_2 to methanol, with hydrogen obtained from renewable energy, has been proposed as a way of solving two of the main problems that technology is currently facing: Need to reduce CO_2 emissions and depletion of fossil fuels. This has already been proposed by G. Olaf [1,2] (Nobel Prize of Chemistry by his work on carbocations) and has been the basis of an extensive research program in Japan [3]. Numerous researchers, as is clear from the various existing reviews, have worked to achieve improvements in the existing catalysts for this reaction [4-11].

One of the drawbacks of this reaction is the low conversion per pass due to the limitations posed by thermodynamic equilibrium [12-14]. In fact, the conversion per pass is even lower than in the conventional process of methanol production from CO+ H_2. Although the industrial process would recycle the unconverted reactants until almost full conversion was achieved, the low conversion per pass would increase the production cost.

The use of membrane reactors has been proposed as a way to improve the methanol yield that can be achieved per pass. This idea was first proposed by Struis et al.[15], using Nafion membranes. The basic idea of this type of reactor is that by removing the reaction products, methanol and/or water, the yield to the desired product can be increased. This concept has been widely employed in dehydrogenation reactions, using Pd membranes, that are permselective to hydrogen [16], but the use of water selective membranes is much less studied. Struis et al. [17] have also investigated by a mathematical model the possibilities of membrane reactor and have proven that it is possible to increase greatly the achievable yield. However, Nafion membranes have the disadvantage that they cannot be used at temperatures above 200 ºC, which significantly limits their application in this reaction, since at this temperature the reaction rate is too low, and would require too large reactors.

The use of zeolite membranes has been proposed in a patent [18] for membrane reactors to obtain methanol. Zeolites, being inorganic materials, can withstand higher temperatures than polymeric membranes. That patent shows by mathematical models that zeolite membrane reactors could provide higher yield to methanol or allow lower operating pressures than conventional reactors. Barbieri et al. [19] used a mathematical model to compare two membranes, one highly hydrophilic and other more hydrophobic, and they found that the hydrophilic was preferable. Gallucci et al.[20] experimentally proved that in a zeolite membrane reactor the conversion could be higher than the conventional fixed bed reactor. This performance improvement is consistent with the mathematical models developed by them authors [21]. Wang et al. [22] have tested zeolite A and SOD membranes in the selective water removal from methano, dimethyl carbonate and dimethylether, thus simulationg their synthesis in membrane reactors with CO_2 as feed. High separation factor were found in the interval 125-200ºC. A related material, alumina-silica composite membrane, was tested by Farsi et al [23] in methanol synthesis by CO_2 hydrogenation.

Zeolite membrane reactors have also been proposed for other reactions, such as Fischer-Tropsch or production of dimethyl ether [24-28]. Despite the interest of the possible applications of zeolite membranes in this type of reactors, there is no extensive study on the permeability and selectivity of zeolite membranes under conditions relevant for methanol production.

Recent work has determined the permeations and selectivities that can be obtained with zeolite A membranes [29]. The objective of this work is to obtain selectivity and permeance values with other types of zeolite membranes under relevant conditions for the hydrogenation of CO_2 to methanol. A preliminary study on the use of a combination of packed bed reactor and a membrane reactor will also be presented.

2. Experimental

2.1. **Zeolite membrane preparation**

- Zeolite A membranes were prepared at Yamaguchi University 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 μm) by a secondary growth method. Supports were immersed in a synthesis mixture having molar ratio of 1 SiO_2:0.5 Al_2O_3:1NaO:75H_2O after applying seed crystals, heated at 100 °C for 4 h. XRD and SEM analyses showed formation of zeolite A membrane on the support. The zeolite membrane was tested in the pervaporation of a mixture water-ethanol, yielding a separation factor over 10000.
- Mordenite membranes were prepared at Yamaguchi University by the method described by Zhu et al [30]
- Zeolite T membranes were provided by Mitsui Zosen Machinery & Service, Inc.
- CHA and Ti-CHA membranes were prepared at Kansai University. High-silica CHA membrane preparation method is based on the method described by Imasaka et al. [31].
- Ti-CHA membranes were prepared by secondary synthesis. The seed crystals prepared by the method described by Imasaka et al. [30]. The synthesis mixture was comprised of colloidal silica (40 wt.%, Aldrich, Ludox AS-40), titanium oxide (TiO2, anatase-type, Wako Pure Chemical Industries, Ltd.), N,N,N-trimethyl-1-adamantammonium hydroxide (TMAdaOH , 20 wt.%, SACHEM) and hydrofluoric acid (HF, 46 wt.%, Wako Pure Chemical Industries, Ltd.) with the molar composition of 1.0 SiO2: 0.033 TiO2: 1.4 TMAdaOH: 1.4 HF: 6.0 H2O. The synthesized gel was then put onto the α-alumina porous

support (average pore size: 0.9 mm, porosity: 0.29, Iwao Jiki Kogyo Co., Ltd.) coated with seed crystals, and the entire support surface was rapped with polytetrafluoroethylene tape. The samples were transferred to an autoclave and heated at 423 K for 72 h. The samples were calcined at 853 K for 12 h to remove the TMAdaOH.

2.2 Characterization of zeolite membranes

The zeolite membranes described in this work were tested towards their capability to separate water from a mixture containing also H_2 and CO_2 at the temperature needed for CO_2 hydrogenation. The zeolite membranes were located in a stainless steel module and sealed with graphite seal rings. The seal rings were made by compressing in the same module a mixture of graphite and silicone grease against a stainless steel tube with the same external diameter as the ceramic support where the zeolite membrane was deposited. The module was located in an electrical furnace with PID control, being the thermocouple located inside the tubular membrane.

The feed was composed by a mixture of H_2, CO_2, N_2 and H_2O. All gases were fed through mass flow controllers and H_2O was metered by an HPLC pump to a stainless steel coil in a sand bath heated to 200 ºC, together with N_2, in order to achieve a steady flow. Ar was used as sweep gas. The products were analyzed by gas chromatography. Then, the experimental separation factors between compounds *i* and *j* (SF_{ij}) were calculated, according to the IUPAC rules, as the ratio of concentrations of those compounds in permeate and retentate (equation 1).

$$SF_{ij} = \frac{[p_i/p_j]_{permeate}}{[p_i/p_j]_{retentate}} \qquad (1)$$

The nitrogen permeance at 1 bar and room temperature was measured for each membrane. Table 1 shows that in all cases it was around 10^{-7} $mol.m^{-2}$-s^{-1}.Pa^{-1}, (and even lower for zeolite A) which implies a high quality of the membranes. The experimental conditions for the permeation tests are summarized in Table 1. H_2/CO_2 ratio in the feed was always 3 and the total pressure was 100 kPa.

Table 1. N_2 permeance and operating conditions for separation experiments

Membrane	N_2 permeance (*) ($mol.m^{-2}$-$s^{-1}.Pa^{-1}$)	Feed cm^3(STP)/min	%H_2O	T ºC	Purge (Ar) cm^3(STP)/min
Zeolite A	$3.88 \cdot 10^{-10}$	275	18	160-260	10
MOR	$6.73 \cdot 10^{-8}$	275	18	160-260	70
Zeolite T	$1.57 \cdot 10^{-7}$	275	18	160-230	70
CHA-Al	$6.58 \cdot 10^{-8}$	169	8	210	70
CHA-Ti	$8.45 \cdot 10^{-8}$	169	8	210	70

(*) At room temperature and 1 bar

2.3. Catalyst

A conventional $CuO/ZnO/Al_2O_3$ catalyst was prepared by co-precipitation of the corresponding salts at constant pH, following literature procedures [32]. The resulting catalyst has a ratio Cu/Zn/Al 45/45/10 and a surface area of 66 m^2/g, similar to other catalysts described in literature. XRD of the precipitate showed the existence of Cu and Zn hydroxi-carbonates, in addition of CuO, ZnO and Al_2O_3. The crystallite size of CuO, calculated by the Scherrer equation was 5-6 nm, which is similar to other studies [33]. The used catalyst contains only Cu, CuO, ZnO and Al_2O_3.

2.4. Permporometry tests

Permporometry was used to obtain information about defects formed in one membrane. This technique implies the measurement of gas permeation with a feed containing variable partial pressure of a vapor that can condense in the pores [34].

The pore size (d_k), in m, is related with the partial pressure of condensing vapor relative to the saturation pressure (P/P_S) by the Kelvin equation:

$$d_k = \frac{-4\sigma \cos\theta}{\nu RT \ln\left(P/P_S\right)} \qquad (2)$$

where σ is the surface tension of the liquid condensate, in $N.m^{-1}$, ν is the molar volume of the liquid, in $m^3 mol^{-1}$, T the absolute temperature in K, and θ the contact angle.

Although this equation is not precise for micropores, it provides some information about the size of defects and their contribution to the total flux.

2.5. Reaction tests

The performance of a traditional reactor (TR), i.e. a packed bed reactor, was compared with the combination of a TR with a zeolite membrane reactor (TR+ZMR). In the second case part of the catalyst is located in the preliminary packed bed reactor and other part inside the tubular membrane. This configuration has the advantage that the gas in the zeolite membrane reactor has always some water, as it comes from the TR, and thus the blockage of pores by water is present in all the length of the zeolite membrane. The exit products were analyzed by gas chromatography.

3. Experimental results

3.1. Zeolite A

A study showing the results with a zeolite A membrane under a variety of operating conditions has been previously published [29]. In order to allow the comparison with other membranes, the effect of temperature on the separation factors H_2O/H_2 and H_2O/CO_2 is shown in figure 1. The increasing separation factor at temperatures below 200ºC suggests that water diffusivity increases with temperature in this interval. The decreasing separation factor at temperatures over 200ºC can be explained by the lower adsorption of water at high temperature, which leaves open pores where permanent gases can flow freely.

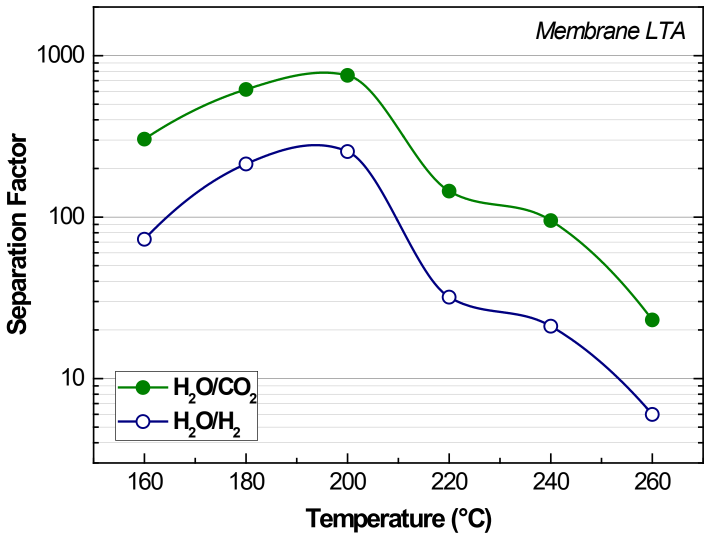
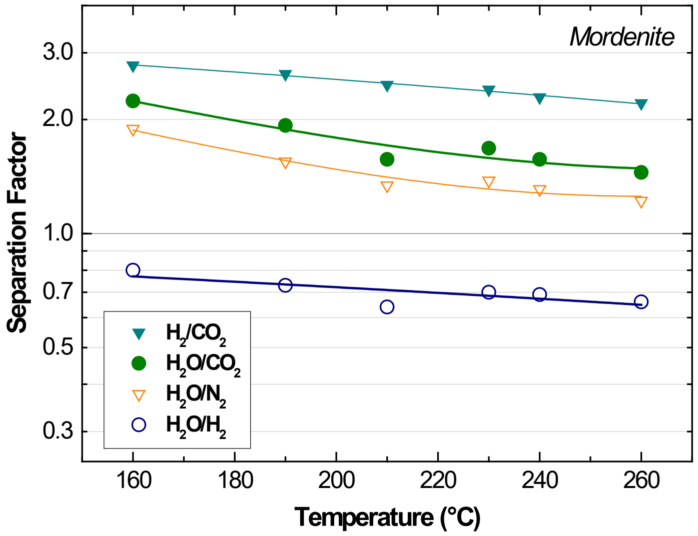


Fig 1. Separation Factor H_2O/H_2 and H_2O/CO_2 with a zeolite A membrane. Lines are only for eye aid.

3.2. Mordenite and Zeolite T membranes

The results of the permeation experiments with mordenite and zeolite T membranes are shown in Figure 2.



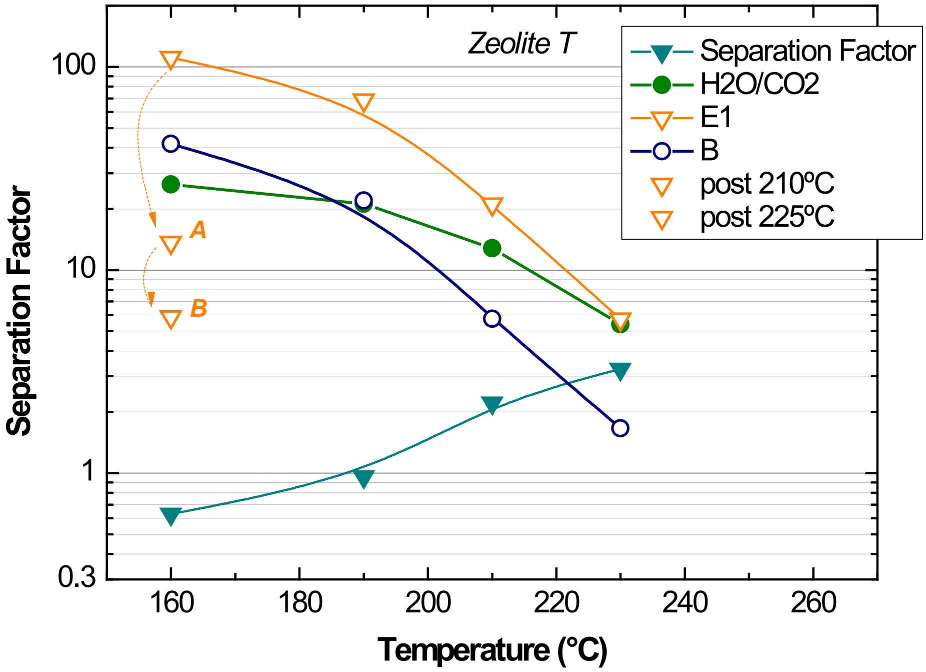


Figure 2. Separation factors with mordenite (up) and zeolite T (down) membranes. Points marked as A and B for zeolite T correspond to H_2O/N_2 selectivity measurements after heating at 210 and 230ºC, respectively. Lines are only for eye aid.

The performance of mordenite membranes was much lower than with zeolite A. In fact, the separation factor (SF) H_2O/H_2 was smaller than 1, implying that hydrogen permeated faster than H_2O. This low value for the SF implies that mordenite membranes obtained by this method can be discarded for their use in membrane reactors for CO_2 hydrogenation to methanol.

3.3. Zeolite T

The results with zeolite T were good a low temperatures and the separation factors were intermediate between those of zeolite A and mordenite (e.g. SF H_2O/H_2 of 26 at 170ºC), but they decreased quickly when the temperature was increased. The SF above 200ºC was too low for their use in membrane reactor for the intended application. In fact, we observed that when the temperature was decreased the SF was not recovered (points A and B in Figure 2 (down)). For example, after heating to 210ºC, the $SF_{H2O/N2}$ at 170ºC was only 17, while before heating it was around 100. These results suggest that heating the membrane caused the appearance of some defects. Another possible explanation is that by heating the membrane, surface OH groups were lost, thus making the membrane less hydrophilic. The zeolite T membrane was characterized by permporometry after use, i.e. by measuring N_2 permeance under variable partial pressure of water at ambient pressure, as aforesaid in the experimental section. This technique is suitable to measure pores of a few nanometers. We found no flux of nitrogen at very low partial pressure of water for the zeolite T membrane before use, indicating the absence of defects. The pores that were detected in Figure 3 are nanometric defects, which probably correspond to the intercrystalline spaces created by heating the membrane. In fact, the defects are smaller than 4 nm, and 69% of the flow is through pores smaller than 2 nm.

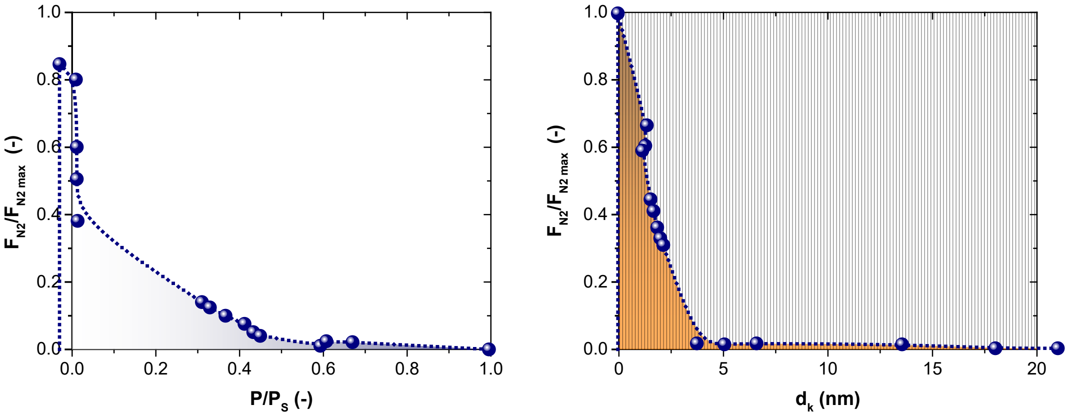


Figure 3. Permporometry results with used zeolite T membrane. Left: ratio of nitrogen flux with dry and humid feeds vs. relative pressure of water. Right: ratio of nitrogen flux with dry and humid feeds vs. pore diameter calculated with the Kelvin equation.

3.4. CHA and Ti-CHA membranes

Chabazite and Ti-Chabazite membranes were tested at the conditions reported in Table 1. The results are given in Figure 4. The separation factors were lower in all cases than those obtained with zeolite A, which again suggests that zeolite A would be preferable for the use in a membrane reactor. However, the H_2/N_2 separation obtained in one case with a Ti-CHA membrane (Ti-2), near 18, is clearly higher than the value corresponding to Knudsen flow (3.7), and thus could be indicative of a potential for further developments. This is interesting because polymeric membranes rarely withstand more than 200ºC and porous membranes rarely provide high separation factors by molecular sieving.

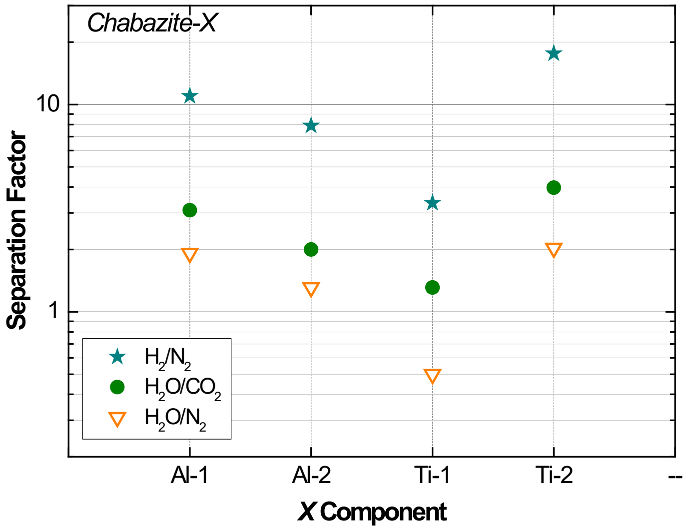


Figure 4. Results obtained with Chabazite (Al-1 and Al-2 membranes) and Ti-Chabazite (Ti) membranes.

3.5. Catalyst performance in TR+ZMR

Comparison of a Traditional Reactor (TR), i.e. a conventional packed bed reactor, and the combination with a membrane reactor (TR+MR) is shown in Figure 5. A zeolite A membrane was employed for this configuration. It may be seen that the combination TR+MR always provided higher yield to methanol than the TR. In fact, in some cases the achieved yield to methanol was higher than the value calculated for the thermodynamic equilibrium. The values of yield were low, because the employed pressure was low, but these results can be considered as a proof-of-concept.

The CO_2 conversion was much larger than the methanol yield. This implies that a large percentage of the converted CO_2 was transformed to CO and H_2O, according to the reverse water gas shift reaction (reaction (r.2)) instead to methanol (reaction (r.1))

$$CO_2 + 3\ H_2 \rightarrow \quad CH_3OH + H_2O \qquad\qquad (r.1)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (r.2)$$

Reverse water-gas-shift also produces H_2O, which is a product of reaction (r.1) and thus reduces the achievable methanol yield. In fact figure 5 shows that in many cases the increase in CO_2 conversion is much higher than the increase of methanol yield, which implies that RWGS was more favored by the removal of water than methanol synthesis. Therefore, a way to improve the results would be by developing a new catalyst more selective to CH_3OH. The conventional catalyst is suitable for operation at high pressure, that favors reaction (r.1), but a new catalyst that reduces the effect of reaction (r.2) would allow profiting the capability of the zeolite membrane for water removal.

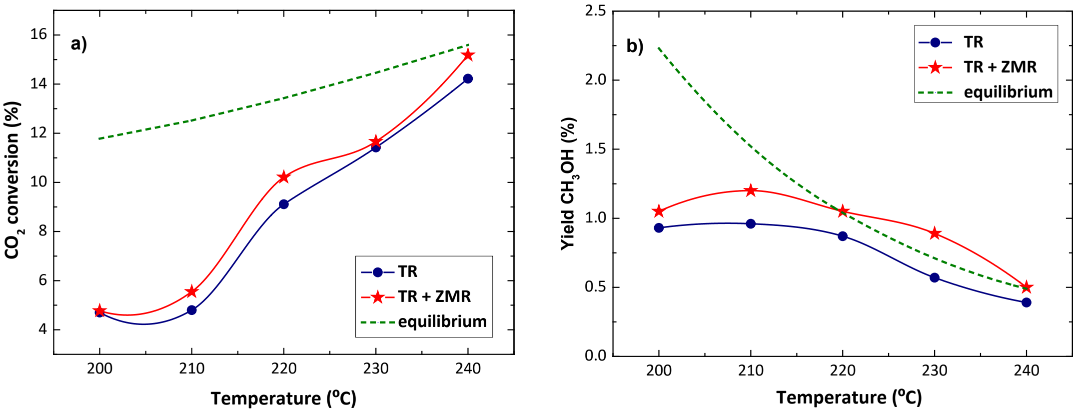


Figure 5. Results obtained in a packed bed reactor and the combination of a zeolite membrane reactor with a packed bed reactor. P= 5 bar; total feed flow rate: 145 cm^3(STP)/min. H_2/CO_2 molar ratio= 3. Lines are only for eye aid.

The comparison of permeances for different gases, calculated from the composition of the permeate in the membrane reactor and the mean partial pressure of each gas in permeate and retentate sides, is shown in Figure 6. These results show that in the actual conditions existing in the membrane reactor the permeance of water was much higher than that of hydrogen, i.e. water was selectively removed from the reaction environment. This observation is another proof of the potential of a zeolite membrane reactor.

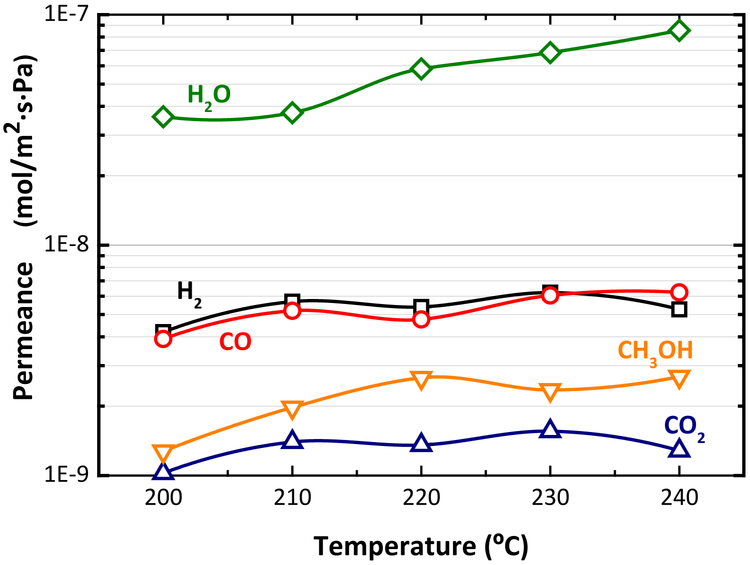


Figure 6. Experimental permeances calculated from the composition of the exit streams of the membrane reactor in actual reaction experiments. Lines are only for eye aid.

4. Conclusions

A study on the separation of water vapor from mixtures containing hydrogen and carbon dioxide, at temperatures that can be expected for methanol production by CO_2 hydrogenation shows that the most promising membrane for its use in a zeolite membrane reactor is zeolite A. The selectivity H_2O/H_2 was higher than that obtained with zeolite T, mordenite, chabazite or Ti-chabazite. The higher permeoselectivity of this membrane is probably related with the high hydrophilicity of zeolite A, which has the highest aluminium content. As a word of caution it is worth to remark that these results are for the membranes compared in this work. It is possible that some of these materials could provide better selectivity with changes in the preparation method.

Preliminary experiments using a zeolite membrane reactor with a zeolite A membrane, show that the combination of a zeolite membrane reactor with a conventional reactor can provide improved performance, with a yield that in some cases is even higher that that corresponding to the thermodynamic equilibrium in a conventional reactor. However, operation at low pressure, which could be one of the advantages of using a zeolite membrane reactor, implies a large contribution from the reverse water gas shift reaction. It increases more the CO_2 conversion than the methanol yield, which is an undesired behavior.

The methanol yield achieved in this work was small, but we think that there is room for improvement. Future work should be addressed towards membranes with improved performance, catalyst with better selectivity to methanol at low pressure and optimization of the global system with realistic mathematical models that include the real behavior of membranes and catalyst.

Acknowledgment

The authors thank the Minister of Economy and Competitiveness (Spain) for financial support for the project CTQ2016-76533-R.

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