

Article

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Methanol conversion to Dimethyl ether in catalytic zeolite membrane reactors

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Abstract

In this work, two ZSM-5 type zeolite supported membranes were used as a catalytic membrane reactor for dimethyl ether (DME) synthesis *via* MeOH dehydration. The membranes, both commercial and tubular, had the same ZSM-5 zeolite layer, but a different support (TiO_2 and $\gamma\text{-Al}_2\text{O}_3$) and were operated as contactor in through flow configuration.

The performance of the two membrane reactors were analysed as a function of the temperature (150-250°C), feed pressure (120-300 kPa), spanning a wide range of WHSV ($1\text{-}13.3 \text{ g}_{\text{MeOH}} \text{ g}_{\text{Catalyst}}^{-1} \text{ h}^{-1}$) and feed composition (25-100%_{mol} MeOH).

ZSM-5- Al_2O_3 membrane (Si/Al=200; porosity of the zeolite layer=0.2; thickness=50 μm , area=50.6 cm^2) exhibited always a greater conversion than ZSM-5- TiO_2 (Si/Al=200; porosity of the zeolite layer=0.2; thickness=63 μm , area=18.8 cm^2) one, revealing an influence of the membrane support, correspondent to an additional catalytic effect induced by the Al_2O_3 , which further enhanced the DME production. At 200°C and 1 h^{-1} , this reactor achieved a MeOH conversion of $86.6 \pm 6.7\%$, very close to thermodynamic equilibrium conversion. In addition, both membrane reactors showed 100% DME selectivity.

Keywords: Methanol dehydration; ZSM-5; catalytic membrane reactor; DME; membrane contactor

Introduction

Dimethyl ether (DME) production has drawn increasing attention as a promising and clean and environmentally sustainable alternative to diesel fuel, owing to its high cetane number, low auto-ignition temperature, and low emission of pollutants. Currently, more than 65% of the globally produced DME is blended with LPG [1] (liquefied petroleum gas). Combustion of DME/LPG blends shows 30–80% reduction in CO₂ emission and 5–15% reduction in NO_x emission (as compared with the combustion of LPG). Nowadays, DME is mainly used as aerosol propellant in spray cans, replacing the banned ozone-destroying chlorofluorocarbons but, in the last decades, it is receiving a growing attention also as alternative and eco-friendly fuel [2].

DME production from methanol dehydration in gas phase (Eq. 1) is regarded as a promising route and its use in the chemical industries is increasing, also in comparison with liquid phase reaction [3]. It is an exothermic reaction, occurring without variation of mole number. For this reason, it is not thermodynamically affected by reaction pressure, whereas its thermodynamics is favored at low temperature.



DME can be produced in gas-phase via-methanol dehydration, following the indirect or direct synthesis route. Indirect synthesis is a two-steps process: the traditional methanol synthesis from syngas over Cu/ZnO/Al₂O₃ (CZA) redox catalyst, in the temperature range 240–280 °C and pressure between 30-70 bar, followed by methanol dehydration reaction, using acid catalyst, to obtain DME. In the one-step process the two reactions, methanol synthesis (via CO hydrogenation) and the dehydration to DME, take place in the same reactor under process conditions close to those of methanol synthesis. This is a valid alternative for DME production [4, 5] as the use of a bifunctional catalyst (with metallic and acidic functions) allows the synthesis of DME in a single step with the additional benefit of shifting the equilibrium of the synthesis of MeOH by means of the alcohol

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3 dehydration to DME and increasing the conversion of CO consequently, even operating at high
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5 temperatures and low pressures [3].
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8 This single step route can be also promising for the production of MeOH via CO₂ hydrogenation, a
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10 valuable strategy for renewable energy utilization in both chemical industry and power generation,
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12 using, where needed, H₂ produced from renewable energy sources. Under this perspective, the
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14 production of DME from “one pot” catalytic hydrogenation of CO₂ results a promising approach that
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16 well fits the objectives of carbon capture and utilization (CCU) in power and industrial sectors.
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19 As for the acid catalyst, studies were initially carried out with γ -Al₂O₃, exhibiting a high selectivity
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21 in the temperature range 200–300 °C [6] and this material was investigated owing to its low cost,
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23 high surface area, good thermal and mechanical stability. Furthermore, γ -Al₂O₃ shows high selectivity
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25 to DME even at a high temperature (up to 400 °C) thanks to the presence of weak Lewis acid sites
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27 able to hinder side reactions [7]. On the other hand, γ -Al₂O₃ suffers of a main drawback, which is the
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29 catalyst deactivation induced by water presence [8] that suggested, years ago, the use of zeolites as
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31 acid catalysts (H-ZSM-5, H-Y, H-ZSM-22) [9,10].
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35 In fact, the presence of water, reaction product, significantly deactivates the catalyst, owing to the
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37 blocking of the active sites by its molecules. In this concern, zeolites (ZSM-5, BEA, FER) were also
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39 investigated as alternative to γ -Al₂O₃ revealing a better stability to water presence and good
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41 conversion and selectivity. In addition, these materials offer the possibility to modulate the catalyst
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43 properties (acidity, specific surface area, crystal size and shape selectivity) as a way to improve the
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45 process performances. Nevertheless, in the temperature range of direct synthesis (260–300 °C), the
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47 acid catalyst may start to promote other reactions, converting the methanol to a range of different
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49 hydrocarbons, such as poly-methylbenzenes, which constitute coke [7]. On the light of this
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51 considerations, it is still a considerable challenge to develop new strategies to simultaneously enhance
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53 the conversion and selectivity of methanol dehydration to DME, limiting phenomena such as catalyst
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55 deactivation induced by water presence.
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3 Catalytic membrane reactors are today a promising solution for several processes involving chemical
4 and petrochemical industry, biotechnology and environmental protection, energy conversion,
5 hydrogen production and well fulfill the requirements of Process Intensification and Green
6 Chemistry, offering better performance, lower energy consumption, lower volume occupied with
7 respect to the conventional operations, etc. [11,12,13,14]. Today, the redesign as membrane systems
8 of traditional operations is concretely contributing to finalize the goals of the process intensification
9 and green chemistry by a new “green process engineering”, in many sectors. Membrane reactors
10 constitute the most significant class of the so-called “multifunctional reactors”, since in various cases,
11 the combination of both separation and reaction in the same unit, allow to significantly reduce the
12 number and the size of reaction/separation units [11,13,15, 16].
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15 Membrane reactors find large room of applications also as contactors, for optimizing the contact
16 among reactants and catalyst, in most of the cases immobilized in the membrane or deposited on one
17 side of it. Recently, few literature articles have reported about the use of zeolite membranes for the
18 in-situ H₂O removal in a packed-bed membrane reactor [17,18, 19]. Volkov et al. [20] reported about
19 the use of a catalytic membrane constituted by F-4SF onto the internal surface of the ceramic
20 ultrafiltration tubular membrane. Fedosov et al. [21] studied the MeOH dehydration in a membrane
21 reactor containing a NaA zeolite membrane used for removing water from reaction volume,
22 constituted by a catalytic bed of γ -Al₂O₃. In 2016, Zhou et al. [22] developed a sandwich FAU-LTA
23 zeolite dual-layer membrane, which they used as a catalytic membrane reactor for the synthesis of
24 DME, preventing the catalyst deactivation through the selective and continuous removal of the
25 generated water from the reaction system.
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28 Inspired by the findings reported in literature about the good stability of zeolite catalysts toward water
29 and coupling with the positive assets offered by catalytic membrane contactors, in this work, we used
30 a catalytic zeolite membrane reactor as a contactor for the DME production by MeOH dehydration.
31 We used the membrane reactor in “through flow” configuration, thus letting pass the whole feed
32 through the membrane and having only the permeate as outlet stream. This choice was done
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3 considering that the passage of a continuous flow through the catalytic membrane could promote the
4 removal of water from catalytic sites, reducing the catalyst deactivation that is usually observed in
5 traditional catalytic beds. In addition, the use of membrane contactor offers additional advantages
6 with respect to a traditional reactor such as an enhanced mass transfer rate of reactants, a better
7 exposition of catalyst surface area, the possibility of tuning the contact between reactants and
8 catalyst, the reduction of catalyst particles aggregation and a better control of fluid-dynamics,
9 together with a major compactness.

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19 Two commercial membranes having the same ZSM-5 zeolitic layer, but a different support (TiO₂ and
20 γ -Al₂O₃), were used, aiming at investigating also if the support can affect MeOH conversion and
21 DME selectivity. While TiO₂ should not have a catalytic activity toward this reaction, γ -Al₂O₃ is
22 instead recognized as a good catalyst for this reaction, even though this material shows a tendency to
23 be de-activated by water presence. The performance of the catalytic membranes was investigated as
24 a function of the temperature (150-230 °C), feed pressure (120-300 kPa), weight hourly space velocity
25 (1-13.3 g_{MeOH} g_{Catalyst}⁻¹ h⁻¹) and feed composition (25-100 mol% MeOH).
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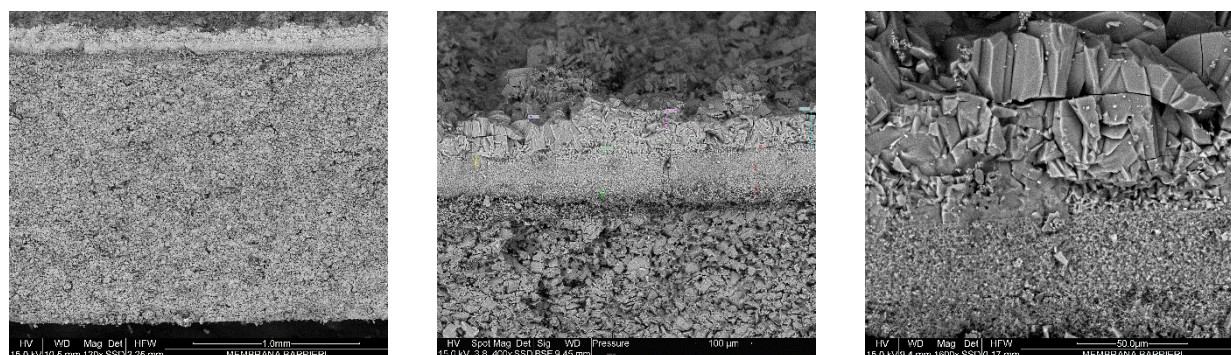
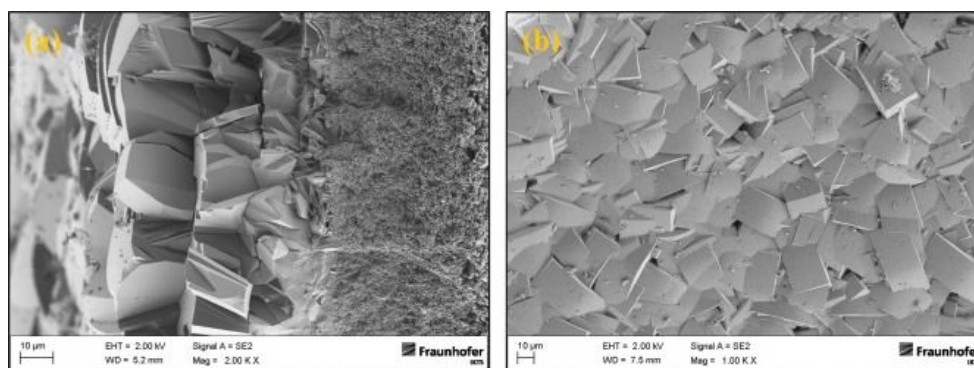
35 36 **Materials and methods**

37 38 39 *Membranes and reaction set-up*

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41
42 Table 1 summarizes the characteristics of two different tubular ZSM-5 supported membranes, which
43 were supplied by Fraunhofer – IKTS. Both membranes are constituted of selective membrane layer
44 of ZSM-5 with a Si/Al ratio of about 200 and porosity of 0.2. The first membrane has the ZSM-5
45 layer deposited on TiO₂-support (support tubes and intermediate layers made of TiO₂); whereas the
46 second one has ZSM-5 layer over γ -Al₂O₃. The pore size of the zeolite layer, is ca. 100 nm (Figure 1
47 and Figure 2) for both composite membranes. SEM pictures of ZSM-5-Al₂O₃ membrane were
48 reproduced from literature to avoid the membrane breaking as the showed SEM pictures are
49 representative of the membranes used in this work.
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Table 1 – Membrane and membrane reactor characteristics

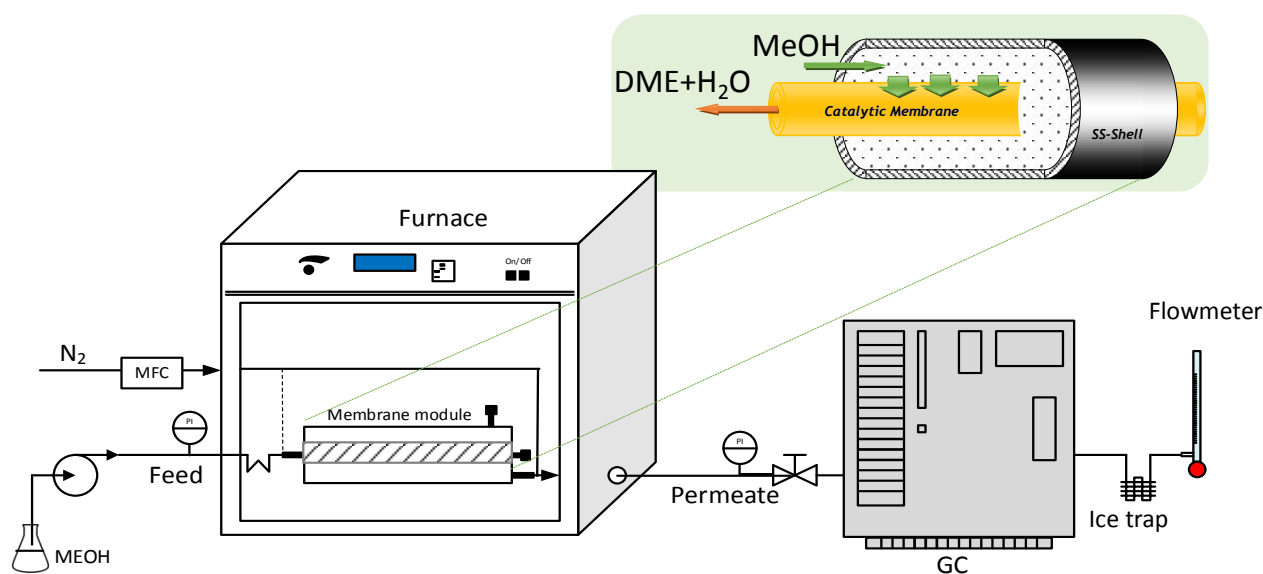
<i>Membrane materials</i>	<i>ZSM-5 on TiO₂</i>	<i>ZSM-5 on Al₂O₃</i>
<i>Si/Al ratio</i>	200	200
<i>Porosity of the zeolite layer</i>	0.2	0.2
<i>Thickness of membrane layer</i>	63 micrometers	50 micrometers
<i>Reaction Volume (volume of zeolitic layer)</i>	95 mm ³	202 mm ³
<i>Membrane Area</i>	18.8 cm ²	50.6 cm ²
<i>Density of the ZSM-5 catalytic layer</i>	960 g cm ⁻³	960 g cm ⁻³
<i>Length</i>	7.5 cm	23 cm
<i>Inner Diameter</i>	0.8 cm	0.7 cm

Figure 1 – SEM pictures of ZSM-5-TiO₂ zeolite membrane (a) 120x, (b) 400x, (c) 1600xFigure 2 – (a) FESEM images of ZSM-5-Al₂O₃ zeolite membrane. Reproduced from [23] with permission of Elsevier.

Each membrane is assembled in a tubular stainless-steel module, with two graphite O-rings *via* mechanical compression. It has to be highlighted that the reactor modules used for the experiments differed only in length, whereas module diameter, membrane diameter, the annulus between the reactor shell and the membrane, the module configuration, the inlet and outlet lines position, the

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3 membrane sealing were the same. To assure an appropriate comparison, we scaled up the reactant
4 and N₂ (when used) flow rate, according to the different catalytic volume, or, in other word, to the
5 different membrane area. For this reason, showed results are not affected by reactor characteristics.
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10 The experimental apparatus used for this investigation is sketched in Figure 3. The reactor is placed
11 inside an electric furnace (Carbolite) to control the reaction temperature. The temperature was
12 measured in the middle of the reactor shell, by using a thermocouple. An HPLC pump (Thermofisher
13 ISO-3100SD) feeds into the membrane module a pure stream MeOH (Sigma Aldrich), which is
14 directly vaporized inside the furnace through a coil. A pressure gauge with a back-pressure controller
15 is placed on the permeate outlet stream of the membrane reactor to regulate and measure the pressure
16 of the system.
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48 Figure 3 – Scheme of experimental set up and membrane reactor.

49 Adapted from Journal of Membrane Science, 492, M. Cersosimo, A. Brunetti, E. Drioli, G. Dong,
50 K. T. Woo, J. Lee, Y. M. Lee, G. Barbieri, “Separation of CO₂ from humidified ternary gas
51 mixtures using thermally rearranged polymeric membranes”, 257-262, Copyright 2015, with
52 permission of Elsevier.
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59 Operating in “through flow configuration”, the reactor has only an outlet stream corresponding to the
60 permeate. In this configuration, the membrane does not have any separating function. The feed stream

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3 is forced through the membrane, where the catalyst MFI layer is deposited on. This results in an
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5 intensive contact between reactants and catalyst, which can be better exploited with respect to a
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7 conventional fixed bed where channeling phenomenon can occur [24].
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10 Once leaving the furnace the permeate stream is maintained above 110°C by means of a heating line
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12 and analyzed by a GC (Agilent 6890N) with two parallel analytical lines, each of which equipped
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14 with two columns: an HP-Plot-5A (to separate permanent gases such as N₂) and an HP-Poraplot-Q
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16 (for other species), both using Argon 5.5 as carrier. The GC sampled the stream by using a multi-
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18 ways valve; among the others, one connection was used as the inlet and another one for the outlet
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20 streams. The calibration of the GC was carried out with standard mixtures containing 10-25-50-75-
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22 90-100% molar of MeOH, other mixtures containing 10 and 25% molar of DME, and others at 10-
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24 25-50-75-90-100% molar of N₂. Standard integration method was used for integrating the area of the
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26 peaks and a calibration table was then created in the OpenLab software for allowing the automatic
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28 calculation of the stream composition. The temperature of the oven was set at 80 °C and after 3.1
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30 minutes increased up to 120°C with a ramp of 10°C /min. The holding time was of 9 minutes. Because
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32 of the small reactor outlet flow rate, a N₂ stream is fed at the permeate exit acting as a carrier, to
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34 assure the stability of the flow rate fed to the GC and, thus, a correct analysis. In other experiments,
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36 a carrier N₂-stream is fed to the reactor together with the reactant, for investigating the effect of
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38 dilution on the reaction conversion and selectivity. A controlled N₂ flow rate was assured by the use
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40 of a mass flow controller (Brooks Instruments).
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46 Before and at the end of all reaction measurements, the membrane permeation performance was
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48 characterized by measuring the permeance of CO₂ and N₂ at 200°C. The unused ZSM-5-Al₂O₃ and
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50 ZSM-5-TiO₂ membranes showed a N₂ permeance of 582 and 320 nmol m⁻² s⁻¹ Pa⁻¹, respectively and
51
52 a CO₂/N₂ selectivity of 1.3, confirming a Knudsen transport mechanism. After the catalytic test, N₂
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54 permeance was equal to 568 and 335 nmol m⁻² s⁻¹ Pa⁻¹ for ZSM-5-Al₂O₃ and ZSM-5-TiO₂,
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56 respectively. It was not possible to carry out permeation measurements with MeOH, since this zeolite
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58 catalyses the alcohol dehydration to DME already at 200°C.
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The flow rate of the gaseous species (DME, N₂) was measured by feeding the outlet stream of the gas-chromatograph to a tubular flow meter for evaluating the permeating flux. An icebox trap, located before the flow meter, retained condensable species (MeOH, H₂O). The reactor performance was evaluated in terms of MeOH conversion (Eq.1) and DME selectivity (Eq. 2):

$$\text{MeOH conversion} = \frac{Q_{\text{MeOH}}^{\text{Feed}} - Q_{\text{MeOH}}^{\text{Outlet}}}{Q_{\text{MeOH}}^{\text{Outlet}}}, \quad \text{Eq.1}$$

$$\text{DME selectivity} = \frac{2Q_{\text{DME}}^{\text{Outlet}}}{Q_{\text{MeOH}}^{\text{Feed}} - Q_{\text{MeOH}}^{\text{Outlet}}}, \quad \text{Eq.2}$$

Table 2 – Operating conditions of reaction measurements

Furnace temperature, °C	150, 200, 220, 230
Feed pressure, kPa	120; 300
MeOH feed flow rate, μL min ⁻¹	4, 5, 8, 13, 25, 44
WHSV, g _{Feed} g _{Catalyst} ⁻¹ h ⁻¹ ,	1; 2.6; 4.6; 5.1; 8.9; 9.9; 13.3

The operating conditions used for the experiments are reported in Table 2. A methanol stream was converted in a membrane reactor in the temperature range 150-230 °C analyzing, in particular, the effects of variation in feed pressure and WHSV. In the specific case of this work, WHSV (Eq. 3) could be related to the velocity of the feed stream in passing through the zeolite catalytic layer. A low WHSV corresponds to high residence time and, thus, favors the contact of the reactant with the catalyst. The catalyst weight was calculated considering the ZSM-5 layer as the catalyst volume by its density.

$$\text{Weight Hourly Space Velocity, (WHSV)} = \frac{\text{Feed weight}}{\text{Catalyst weight}} \frac{g_{\text{Feed}} h^{-1}}{g_{\text{Catalyst}}} \quad \text{Eq. 3}$$

Results and Discussion

As previously mentioned, the aim of this work is the evaluation of the MR performance of two different ZSM5-based membranes on the MeOH dehydration to DME. Comments are also addressed about the effect of the support on the MeOH conversion and DME selectivity. Significant relevance was devoted to the analysis of the performance as a function of temperature spanning a wide range of WHSV and feed composition.

ZSM-5/Al₂O₃ membrane reactor

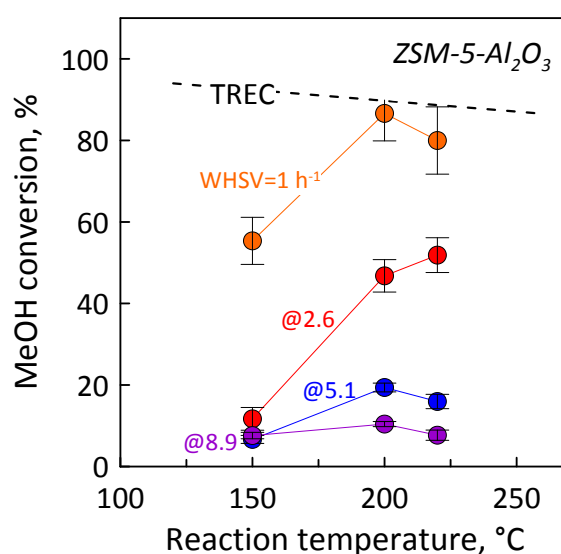


Figure 4 - ZSM-5/Al₂O₃. MeOH conversion in ZSM-5/Al₂O₃ membrane reactor as a function of temperature at different WHSVs. Feed pressure=120 kPa. MeOH feed concentration=100% molar

Figure 4 shows the MeOH conversion as a function of reaction temperature for different WHSVs; the traditional reactor equilibrium conversion (TREC) is also shown for comparison purposes. An increase of MeOH conversion with temperature is observed owing to the effect of kinetic [25, 26]. At WHSV= 1 h⁻¹ the MeOH conversion shows an already significant value (about 60%) at 150°C and the increasing trend is confirmed also at 200 °C (87%), as the theoretical equilibrium value is approached. A further increase in the operating temperature showed a slight drop in conversion down to 80% at 220 °C, most likely ascribable to the thermodynamic effect. However, no catalyst

deactivation was apparently observed as repeating measures in other conditions (e.g., 200°C) the catalytic activity was quantitatively confirmed. The curves obtained by increasing the WHSV showed the same trend but with a reduced impact. In fact, at 8.9 h⁻¹, MeOH conversion was significantly lower than that at WHSV at 1 h⁻¹, with a less pronounced variation, in the same temperature range. It has to be highlighted that DME selectivity was 100% at all the operating conditions considered. As expected, at all the investigated temperatures, a decrease in WHSV enhanced MeOH conversion (Figure 5). The reduction of this parameter leads to a higher residence time and, thus, a longer contact between MeOH and catalyst, thereby promoting the conversion, which ranged from 10.4 to 86.6% as the WHSV decreased from 8.9 to 1 h⁻¹, at 200 °C. Analogous trend was obtained at the other temperatures, confirming the absence of significant advantages on reactor performance for WHSV above 2.6 h⁻¹.

An increase of feed pressure has a negative effect on the MeOH conversion (Table 3). The reaction is not thermodynamically influenced by pressure; therefore, we assume that this evidence can be related to the negative influence of pressure on the desorption of products.

Table 3 – Operating conditions of reaction measurements

WHSV, h ⁻¹	MeOH conversion, %	
	120 kPa	300 kPa
2.6	46.8±4.0	38.3±1.5
5.1	19.4±1.1	16.8±0.3
8.9	10.4±0.63	9.9±0.9

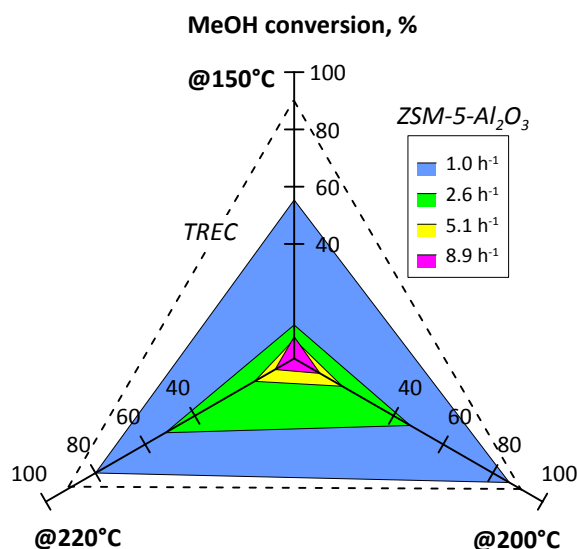


Figure 5 - ZSM-5/Al₂O₃. MeOH conversion as a function of WHSV at different temperatures. Feed pressure=120 kPa. MeOH concentration=100% molar

The effect of reactant dilution was, then, evaluated at 200 °C by feeding a mixture of nitrogen (used as a carrier) and MeOH to the membrane reactor. The temperature value was fixed according to the evidence of the highest conversion at 200°C, the most meaningful condition to investigate the sensitivity of the process to reactant dilution. Setting the MeOH feed flow rate at 10.3 mg min⁻¹ (7.3 mL (STP) min⁻¹), MeOH conversion resulted significantly affected by the presence of N₂ (Figure 6 left), which resulted in an increase of WHSV. The MeOH conversion showed a quite linear dependence on the MeOH feed concentration, passing from 46.8% (in absence of carrier) to 6.7% when diluting MeOH at 26.7% mol (20 mL(STP) min⁻¹ of N₂). To check the effect of N₂ (Figure 6-right), the feed flow rate of carrier was set to 12 mL (STP) min⁻¹ and a decreasing trend in conversion was observed when increasing the MeOH flow rate, mainly as effect of the increase of WHSV.

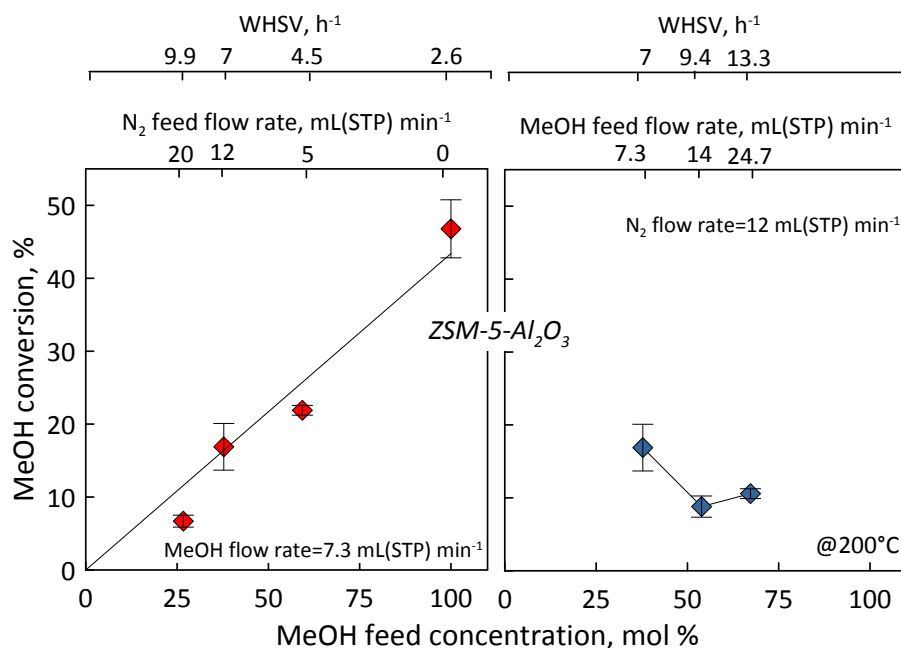


Figure 6 - ZSM-5/Al₂O₃. MeOH conversion as a function of feed concentration. Feed pressure=120 kPa. STP: standard temperature (0°C) and pressure (100 kPa)

Figure 7 summarizes all the measurements performed at 200 °C, highlighting the effects of WHSV and dilution on MeOH conversion. WHSV results the most effective variable, implying a significant reduction of the conversion when it increased; then MeOH concentration reduction, which reflected on reaction rate slowdown and thus can induce a depletion of MeOH conversion, much relevant at the lower WHSV. A feed stream constituted of 1/3 of MeOH led to a conversion of ca. 27.8% (@WHSV= 2.6 h⁻¹) against the 46.8% of conversion obtained when pure MeOH was fed to the reactor. Analogous trend was obtained at a WHSV range of 8.9-9.9 h⁻¹, where MeOH conversion passed from 10.4 to 6.7%. This effect can be ascribable to the slowdown effect on the reaction rate, which is directly proportional to the MeOH concentration in the feed.

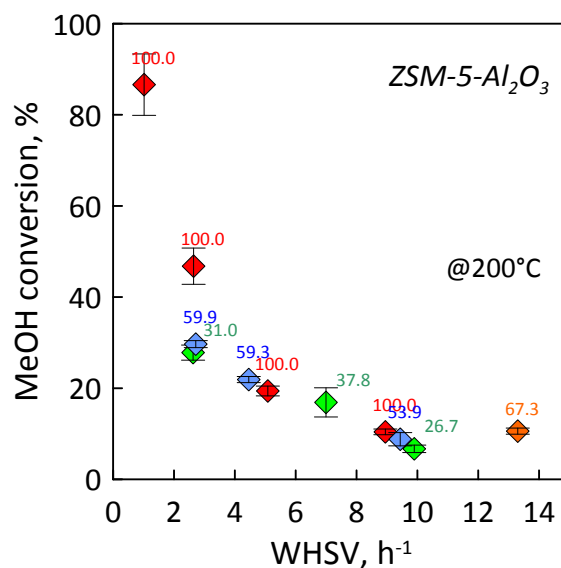


Figure 7 - MeOH conversion as a function of WHSV. Feed pressure=120 kPa. Labels indicate MeOH feed concentration.

ZSM-5/TiO₂ membrane reactor

Analogously to what observed for the γ -Al₂O₃-supported one, ZSM-5-TiO₂ membrane reactor showed an increasing trend of MeOH conversion versus temperature until 230 °C, at all the investigated WHSV (Figure 8). It was not possible to carry out experiments at a WHSV lower than 2.2 h⁻¹, owing to the lower dimension of the membrane, which would have required a lower bottom-scale of MeOH pump.

Overall, MeOH conversion was relatively far from the equilibrium and, at the best, it reached 67% at 220 °C and 2.2 h⁻¹. Also, in this case, the reaction exhibited a full DME selectivity, varying the WHSV from 2.2 to 8.7 h⁻¹, in the temperature range 200-230 °C. At 230 °C, an increment in WHSV (Figure 9) reflected in a reduction of MeOH conversion, which passed from 67% to 11.4% when the WHSV was increased from 2.2 to 8.7 h⁻¹. Similar trends were indeed registered at the other temperatures.

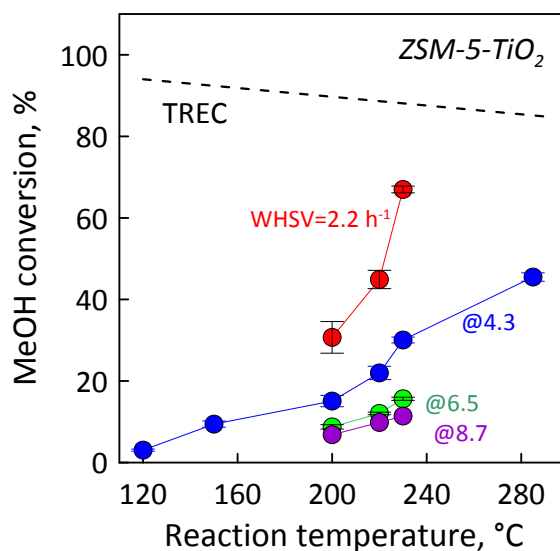


Figure 8 – MeOH conversion as a function of temperature at different values of WHSV. Feed pressure=120 kPa. MeOH feed concentration=100% molar

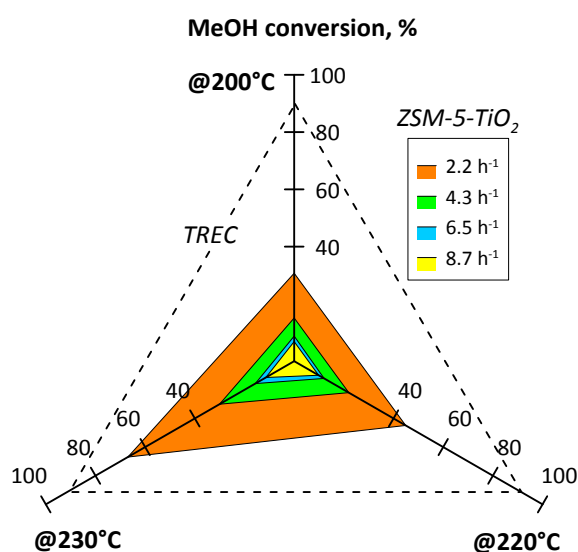


Figure 9 – Effect of WHSV on the MeOH conversion measured at 120 kPa at different values of temperature. The dashed lines connect the equilibrium conversion values at the three temperatures showed on the graph. MeOH feed concentration=100% molar.

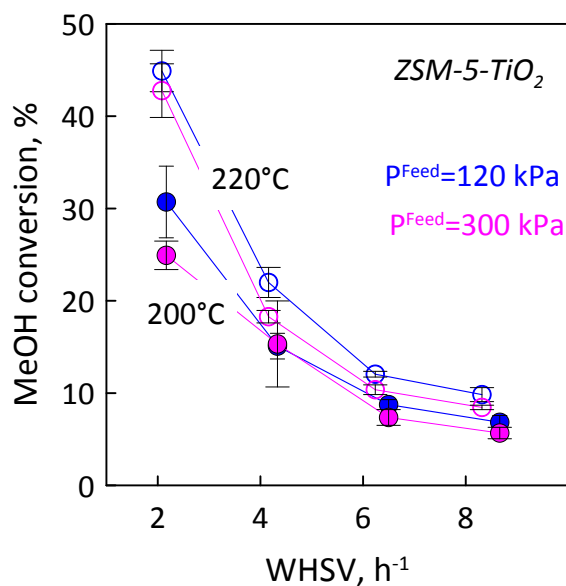


Figure 10 – MeOH conversion as a function of WHSV measured at a feed pressure of 120 and 300 kPa. MeOH feed concentration=100% molar.

Another variable affecting reaction performance is the feed pressure. Analyzing its influence on MeOH conversion at different WHSVs and 200-220 °C, we found an insignificant or even negative effect induced by feed pressure (Figure 10), analogously to what we observed for the ZSM-5-Al₂O₃ membrane reactor. From a thermodynamic point of view, an increment of reaction pressure does not have any influence on conversion since the reaction occurs without variation in mole number. However, the pressure influences the sorption and desorption of reactants and products from catalytic sites, which make these latter not fully accessible for further reactants.

Comparison

Overall, the ZSM-5-Al₂O₃ membrane exhibited a better performance than the TiO₂-supported one, at all the WHSV considered in the experiments, at 200 and 220 °C (Figure 11). This advantage was much more relevant at the lowest WHSV, reaching a MeOH conversion up to 1.5 times higher than the one obtained with ZSM-5-TiO₂ membrane at a WHSV of 2.2-2.6 h⁻¹. In fact, ZSM-5-Al₂O₃ membrane allowed to obtain the highest production of DME equal to 2.07 mL (STP) min⁻¹, at 220°C and 2.6 h⁻¹, feeding 13 μL min⁻¹ of pure MeOH. This suggests that also the type of membrane support

plays a role in the final performance, as in the case of Al_2O_3 , which seems to further promote MeOH conversion. Most likely, the $\gamma\text{-Al}_2\text{O}_3$ support exerted an additional catalytic activity to that of ZSM-5, enhancing the conversion, also considering that $\gamma\text{-Al}_2\text{O}_3$ is a well-known catalyst for this reaction. Contrarily TiO_2 did not actively contribute to the reaction, which was thus catalyzed only by ZSM-5. Further investigations on supports activity needs anyway to be performed to better clarify this aspect.

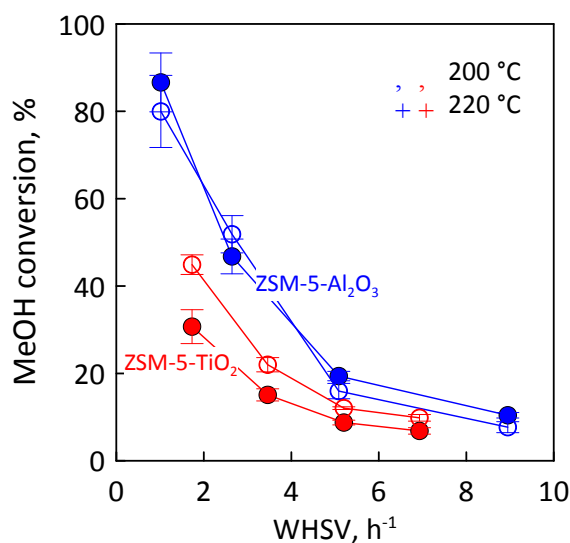


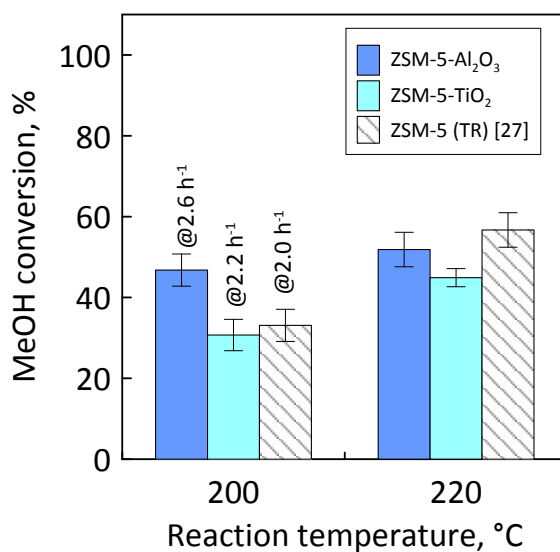
Figure 11 – MeOH conversion as a function of WHSV for the two MRs at 200 and 220 °C. Feed pressure=120 kPa. MeOH feed concentration=100% molar.

Figure 12 shows the MeOH conversion of the two membrane reactors and a traditional reactor (TR) reported in the open literature [27], this latter also constituted by ZSM-5 catalytic pellets, with a Si/Al ratio of 38. The literature result [27] here reported on TR has the own scope to clarify how a membrane reactor behaves, in comparison to a traditional reactor. A more systematic and tight comparison would require the same reaction conditions and same Si/Al ratio of that of membrane reactors, but the quantitative performances comparison with a traditional reactor was out of the scope of this work.

At 200 °C, despite the difference in acidity with TR, ZSM-5- Al_2O_3 membrane leads to a higher conversion with respect to the other two reactors, whereas this effect seems to disappear at 220 °C as the performance of TR was slightly better than the catalytic membrane reactors. However, it needs to

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3 be considered that the measurements were carried out at a slightly different WHSV. Comparing the
4 two membrane reactors, the conversion obtained with the ZSM-5-Al₂O₃ membrane reactor was about
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6 1.8 and 1.3 times greater than that achieved with the ZSM-5-TiO₂ membrane at 200 and 220 °C,
7
8 respectively. This enhanced conversion can be ascribable to an additional catalytic activity exerted
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10 by the Al₂O₃ support, which further promoted the conversion with respect to the membrane supported
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12 by TiO₂. Most likely, also the presence of acid sites on alumina support could give additional activity
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14 of the H-ZSM-5 layer. A full DME selectivity was obtained with both MRs, contrarily to what
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16 reported for TR which selectivity was 96-97%.

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21 Contrarily to what happens in a traditional reactor, the catalytic membrane configuration operated in
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23 through flow is such that the catalyst is continuously exposed to a permeating flux. This can limit the
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25 deactivation of the catalytic sites, promoting the continuous removal of reaction products (DME and
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27 water) and depleting the secondary reactions.



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49 Figure 12 – MeOH conversion as a function of temperature for the two MRs and a TR (adapted from
50 [27]). MeOH feed concentration=100% molar.

51 52 53 54 **Conclusions**

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57 Here we proposed a novel reactor set-up for the synthesis of dimethyl ether via methanol dehydration
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59 based on catalytic zeolite membrane reactor operated as a contactor. We analyzed the performance
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3 of two membranes, having the same catalytic layer, based on ZSM-5 structure and two different
4 supports: Al₂O₃ and TiO₂.

7 At all the investigated conditions, both membrane reactors exhibited full DME selectivity. Overall,
8 the ZSM5-Al₂O₃ membrane behave better than ZSM5-TiO₂, reaching a conversion 1.5 and 1.2 time
9 greater than that achieved with the ZSM-5- TiO₂ membrane at 200 and 220 °C, respectively. The best
10 performance was achieved at 200 °C and 1 h⁻¹, obtaining a conversion of 86.6 %, very close to
11 equilibrium one.

12 MeOH conversion resulted significantly affected by the presence of N₂ in the feed, which induced
13 not only a variation of WHSV, but a depletion of reaction rate owed to the dilution of MeOH
14 concentration. As a consequence, when the feed stream was diluted with 70% of N₂, MeOH was about
15 27.8% (@WHSV= 2.6 h⁻¹) against the 46.8% of conversion obtained when pure MeOH was fed to
16 the reactor.

17 ZSM5-TiO₂ membrane was overall less performant than the ZSM5-Al₂O₃ one, reaching a maximum
18 conversion of 67% at 230 °C. An increment of feed pressure led to lower conversions, most likely
19 ascribable to a negative effect on desorption of reactants and products from catalytic sites.

20 Globally, the reported results showed that MeOH conversion and DME selectivity obtained with both
21 membrane reactors were better than that achieved with a traditional reactor. This fact can be attributed
22 to a positive effect of the continuous exposition of the catalytic layer to a gas flow, which favors the
23 removal of species (i.e. water) from catalytic sites, thus limiting catalyst deactivation and depleting
24 secondary reactions.

25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 **Acknowledgements**

53
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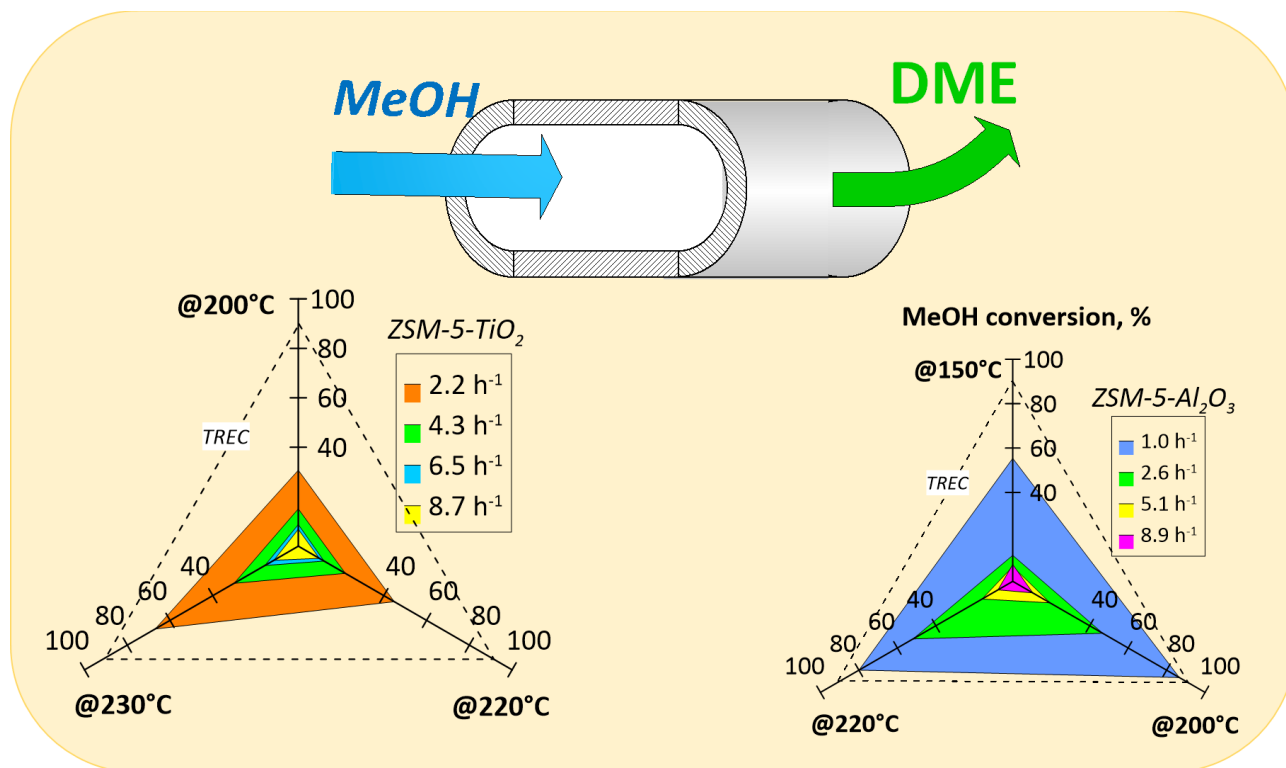
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**Synopsis:**

The novel membrane reactor based on catalytic ZSM-5 zeolite membranes showed good performance achieving a conversion of 86.6 %.