



# Methanol dehydration in NaA zeolite membrane reactor



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## ABSTRACT

Catalytic dehydration of methanol was studied in a reactor with inert, selectively permeable walls made of NaA zeolite membranes. Zeolite layer was synthesized on the flat metal–ceramic support by the in situ crystallization method resulting in selective and thermally resistant membrane. The separation factor of the model water/methanol mixture in the temperature range of 150–250 °C varied from 22 to 5 and the permeate flux of 0.6 kg h<sup>-1</sup> m<sup>-2</sup> was reached. Dehydration of methanol to dimethyl ether was carried out in flow mode in the membrane reactor, using  $\gamma$ -alumina catalyst. The effect of temperature, WHSV, feed pressure and flow rate of a sweep gas on methanol conversion was analyzed. The maximal conversion reached in the zeolite membrane reactor (ZMR) at 250 °C was 88% which is higher than in a conventional reactor by 8%.

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## 1. Introduction

Catalytic processes with selective removal of desired reaction products or by-products from reaction area have always been of interest [1]. The development of selective inorganic membranes with high thermal and chemical stability expands this approach to the intensification of various commercially important processes. Zeolite membranes with pores of molecular size have been studied in a wide number of reactions with thermodynamic or kinetics limitations [2]. The regular pore systems of zeolites with molecular dimensions provide size- and shape-selectivity of membranes. Besides, different affinity of zeolite materials to feed and products promotes selective separation. Today, successful operation of ZMR has been demonstrated on the laboratory scale [3]. Scaling up these projects requires additional optimization of synthetic methods of membrane production and the design of membrane reactors. Industrial application of NaA membranes in alcohols dewatering [4] is a promising example of this material application in membrane reactors. High performance of NaA membrane in water/organics separation is due to zeolite structure with pores of 0.4 nm and its strong hydrophilic properties [5]. Membranes with a defect-free zeolite layer demonstrate water/organics separation factors above 10,000 [6]. In the last decade a number of research works on esterification [7], etherification [8] and condensation [9] reactions assisted with NaA membranes were published. The yield above the thermodynamic limit and significant

improvement of selectivity were demonstrated. However operating temperature for these reactions was not higher than 150 °C. The present work is focused on methanol dehydration to dimethyl ether (DME) in a membrane reactor equipped with NaA membranes operating in the temperature range of 150–250 °C.

Currently, DME is regarded as a clean high-efficiency diesel fuel and LPG alternative [10,11]. The main way to DME production is methanol dehydration



This process is usually conducted in a fixed bed reactor with 80–85% conversion in a temperature range of 250–400 °C on pure  $\gamma$ -alumina or  $\gamma$ -alumina modified with phosphates or titanates [12–15]. The activity of these catalysts is significantly affected by adsorption of water molecules, formed during the reaction, on catalyst active sites [16]. Membrane technologies can be applied to reduce this negative effect. Thus, Sea and Lee reported on water-selective alumina–silica membranes to remove water from the reaction zone; thus preventing the decline of  $\gamma$ -alumina catalytic activity. They demonstrated that use of membranes increased DME yield from 68% in a conventional packed bed reactor to 82.5% at 230 °C [17]. Farsi and Jahanmiri [18] modeled DME synthesis in a membrane reactor with alumina–silica membrane and  $\gamma$ -alumina catalyst. According to modeling results, methanol conversion could be improved from 80% in an adiabatic reactor to 86.2% in a membrane reactor at optimal conditions. Another application of membranes in catalysis was demonstrated by Volkov et al. [19]. A polymeric/ceramic membrane with Nafion-analog catalytic layer results in 37% methanol conversion in flow-through mode at 180 °C. This approach provided stable DME yield due to removal of

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water, in contrast with the packed bed regime [20], where the initial 25% conversion dramatically decreased to 0.3%.

In this work, for the first time, methanol dehydration was performed in ZMR with NaA membranes using  $\gamma$ -alumina catalyst, in a wide range of reaction temperatures, contact times and feed pressures.

## 2. Experimental

### 2.1. Membrane preparation

The NaA zeolite layer was prepared on a stainless steel wire mesh support containing intermediate layer of composite ceramic (mainly titania) with a mean pore diameter of 0.3  $\mu\text{m}$  and average thickness of 40  $\mu\text{m}$  supplied by “ASPEKT” Association (Russia). This structure of the substrate provided for both flexibility and mechanical strength of zeolite membrane. Prior to zeolite layer synthesis the support was cleaned in acetone by ultrasonication for 20 min and dried at 120  $^{\circ}\text{C}$  for 1 h. The metallic side of the support was protected with Teflon tape and then it was placed vertically in Teflon holder. Crystallization of the zeolite on the support was performed in situ from a clear solution of the following composition: 50Na<sub>2</sub>O:5SiO<sub>2</sub>:1Al<sub>2</sub>O<sub>3</sub>:1000H<sub>2</sub>O, at 50  $^{\circ}\text{C}$  for 20 h. Fumed silica (SE “Kalush Test Experimental Plant”, Ukraine) and NaAlO<sub>2</sub> (Riedel-de Haen AG) were used as the source of Si and Al, respectively. Synthesized samples were rinsed with deionized water and dried overnight at room temperature. The procedure was repeated 2–3 times to form a continuous coating.

Synthesized membranes were analyzed by XRD (Rigaku 2500 D-max) using CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) in 2 $\theta$  range of 5–70 $^{\circ}$ . The morphology of the zeolite layer was studied by scanning electron microscopy (SEM, Leo Supra 50VP) with accelerating voltage 5–20 kV and magnification of 1000–25,000. Gas permeation was used as a test for a defect-free layer [21]. The detection limit of the gas permeance was  $2.7 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ . Before the permeation test membranes were pretreated by N<sub>2</sub> flow sweeping in the feed side and evacuation from permeate side to 1 mbar at 70  $^{\circ}\text{C}$ . For membranes free of voids and cracks no N<sub>2</sub>-permeance was detected, because all zeolitic pores were filled with adsorbed water. Membranes were used in the form of disks with 4 cm diameter.

### 2.2. Membrane reactor

Water/methanol separation and methanol-to-DME catalytic experiments were performed in a stainless steel reactor (MR) shown schematically in Fig. 1. The body of MR forms reaction volume of cylindrical geometry with two membranes as its bases. Inlet and opposite outlet are situated on the lateral surface. The ratio of membrane area to reactor volume is 200  $\text{m}^{-1}$ . Two side covers fix the membranes and provide transport of the permeate. Flat rings of fluorinated rubber are used as sealing elements. Reactor covers are connected to a vacuum pump, which allows evacuation of the permeate side to 1 mbar. Permeate was collected in traps, cooled with liquid nitrogen, and was analyzed by GC. In some experiments, evacuation was substituted by sweep gas (He) flushing permeate. Temperature was maintained by an electric oven equipped with a temperature controller and thermocouple placed inside the reactor. Liquid feed is delivered to the system by syringe-pump. Feed, permeate and products were analyzed by GC («Crystal 2000 M») Chromatek, Russia) equipped with a Porapack Q column and TCD detector.

### 2.3. Separation and catalytic experiments

For separation experiments, the mixture of water and methanol (1:1 weight ratio) was fed to the reactor in the temperature range of 150–250  $^{\circ}\text{C}$  at a rate of 2  $\text{g h}^{-1}$ .

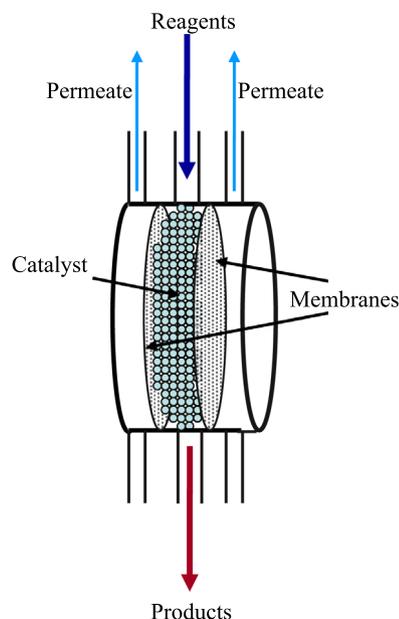


Fig. 1. Schematic diagram of MR operation.

The flux through membrane  $Q$ , separation factor  $\alpha$  (water/methanol) and rate of water recovery  $R$  were calculated as follows:

$$Q = m_p / At \quad \alpha_{W/M} = \frac{x_W / x_M}{y_W / y_M} \quad R = \frac{Q_p^W}{Q_f^W} \times 100 \quad (2)$$

where  $m_p$  is the weight of permeate,  $t$  – experimental time,  $A$  – membrane area,  $x_i$  – weight fraction of component  $i$  in permeate and  $y_i$  – in feed,  $Q_p^W$  – water flux through membrane,  $Q_f^W$  – water flux in feed.

Catalytic experiments were conducted at the following conditions: temperature range 150–250  $^{\circ}\text{C}$ , WHSV 0.5–2.6  $\text{h}^{-1}$ , permeate pressure 1 mbar, sweep flow up to 180  $\text{ml min}^{-1}$ , feed pressure 1.0–1.7 bar. The  $\gamma$ -alumina catalyst was provided by UOP (pellets of 0.25–0.5 mm, BET surface area 220  $\text{m}^2 \text{g}^{-1}$ , pore volume of 0.52  $\text{ml g}^{-1}$ ). 2 g of the catalyst was loaded in the space between membranes. Methanol was fed downflow. Reaction products were cooled in a water heat exchanger and dissolved in ethanol for homogenization. Permeate was evacuated or swept with inert gas. Blank catalytic experiments were run at the same conditions except permeate elimination. In this case membranes played the role of impermeable reactor walls; this regime was regarded as conventional packed bed mode (PB). Compositions of permeate collected in cold traps (liquid nitrogen) and products collected in the ethanol trap were analyzed by GC. Conversion of methanol  $X$  in both ZMR and PB modes was determined as follows:

$$X(\text{PB}) = \frac{m_M^{\text{in}} - m_M^{\text{out}}}{m_M^{\text{in}}} \times 100, \quad X(\text{ZMR}) = \frac{m_M^{\text{in}} - m_M^{\text{out}} - m_M^{\text{perm}}}{m_M^{\text{in}}} \times 100, \quad (3)$$

where  $m_M^{\text{in}}$ ,  $m_M^{\text{out}}$ ,  $m_M^{\text{perm}}$  – mass flowrates of methanol in the inlet and outlet of reactor and passed through membranes, consequently. DME and water were the only reaction products observed in both PB and ZMR regimes of catalytic experiments.

## 3. Results and discussion

### 3.1. Membrane characterization

Synthesis of NaA layer was developed as a simple and reproducible method: crystallization occurs from a clear solution at 50  $^{\circ}\text{C}$ . All

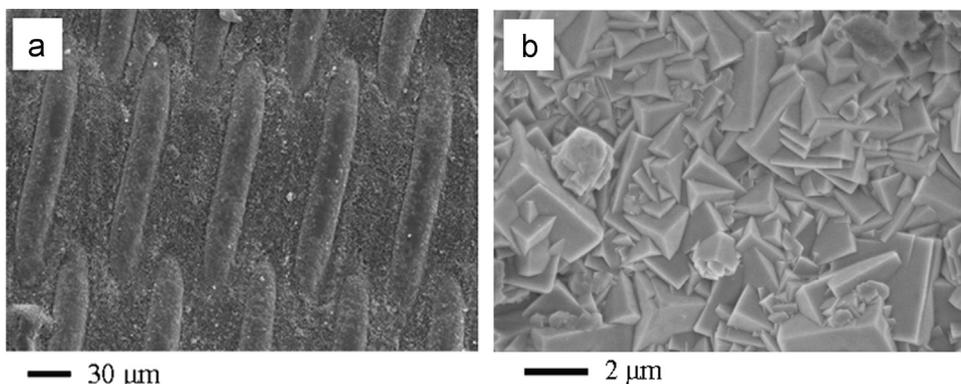


Fig. 2. Typical SEM images of support surface (a) and membrane top surface (b).

samples of membrane materials were tested for cracks and defects using a gas permeability test. The samples impermeable for nitrogen were chosen for further separation and catalytic experiments.

The evidence of continuous zeolite layer formation was attained from SEM images of the membrane surface (Fig. 2). The support was coated with fully intergrowth cubic crystals of size from 0.5 to 3  $\mu\text{m}$ , typical for NaA zeolite. The layer thickness (not shown) was about 20  $\mu\text{m}$ . XRD analysis revealed that the top-layer of membranes is pure NaA phase with LTA structure.

In contrast to the procedure developed by Lee et al. [17] for making inorganic water-selective membrane for methanol dehydration, which requires a three-stage method for gradual silica and  $\gamma$ -alumina deposition followed by heat-treatments of 600–900  $^{\circ}\text{C}$ , simple procedures for the synthesis of NaA membranes e.g. in [6] and in this work have benefits from a technological point of view. In addition, zeolitic coating provides molecular-sieving properties of a membrane.

### 3.2. Separation of water/methanol vapors

The size of methanol and water molecules is 0.296 nm and 0.380 nm, respectively [22], which allows both molecules to pass through a NaA zeolite pore system having pore size of 0.4 nm. In this case, the strong hydrophilicity of the NaA zeolite becomes the main factor for preferential water permeation through a membrane.

Temperature dependence of selectivity and permeation flux of membranes was estimated in separation tests of a model water–methanol feed (1:1 by weight). Fig. 3 shows total permeation flux and its composition as a function of temperature. The total flux is  $\sim 0.6 \text{ kg m}^{-2} \text{ h}^{-1}$  and it is almost independent on temperature. At the same time, water fraction in permeate decreases with temperature, corresponding to reduced separation factor. These data were reproduced in 4 series of measurements in heating–cooling cycles. It allows to suppose a non-destructive character of temperature factor on the membranes at least up to 250  $^{\circ}\text{C}$ . High thermal resistance of the membranes could be due to the composite structure of the flexible support and interconnection of zeolite and intermediate layers which prevent delamination described in [23]. In contrast, the most of NaA membranes on traditional supports, e.g. alumina, are stable only up to 150  $^{\circ}\text{C}$  [24].

At 150  $^{\circ}\text{C}$ , the water/methanol separation factor  $\alpha$  is equal to 22, and decreases to 5 with raising the temperature to 240–250  $^{\circ}\text{C}$ . This effect is related to the smaller difference between water and methanol adsorption at high temperatures and, as a result, lower coverage of the zeolite surface with water. However, the rate of water recovery  $R_w$  decreases slightly with temperature, from 72% to 60% (Fig. 4). Since it remained at a rather high level even at high temperature, high efficiency of NaA zeolite membranes in ZMR should be expected.

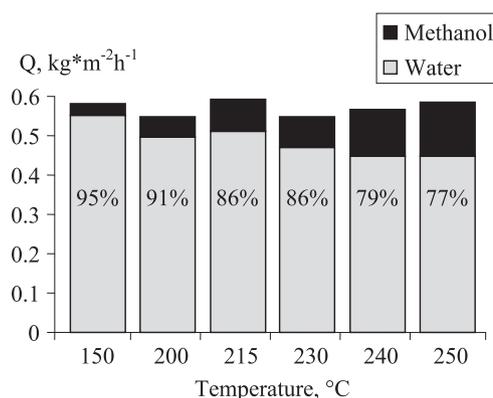


Fig. 3. Permeation flux and permeate composition (wt%) vs. temperature in the separation of model water–methanol (1:1) mixture.

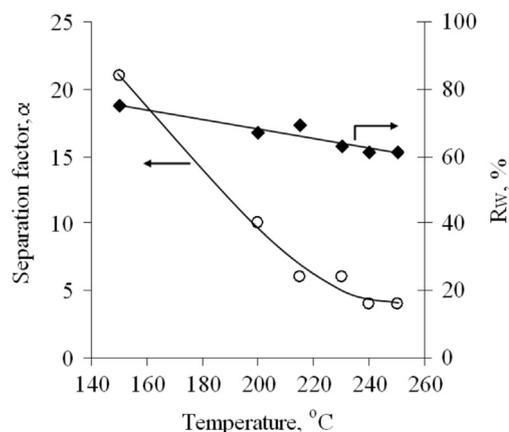


Fig. 4. Temperature dependence of separation factor  $\alpha$  and the rate of water extraction  $R_w$  in water/methanol separation.

The permeance and the selectivity values of the NaA membrane are in accordance with the best characteristics of ceramic membranes at the same conditions [17], namely an alumina–silica membrane with enhanced concentration of acid sites. This fact points to the higher importance of adsorption in water/methanol separation than the molecular sieving effect.

### 3.3. Methanol conversion in zeolite membrane reactor

#### 3.3.1. Permeate elimination regimes

As a first step of the study, the effectiveness of different methods of permeate elimination such as evacuation and sweeping was

tested. These experiments were run at 230 °C and WHSV 0.7 h<sup>-1</sup> with  $\gamma$ -alumina catalyst, loaded between two membranes. In the packed bed (PB) regime, methanol conversion was generally about 30%. Evacuation of the permeate side up to 1 mbar led to a quick increase of conversion to 55%. Decrease of water concentration over the catalyst results in a shift of the competitive water/methanol adsorption equilibrium on active sites to methanol adsorption; thus favoring its additional conversion. Berčić and Levec reported the rate equation for the dehydration reaction of methanol over  $\gamma$ -alumina, which represents the kinetic behavior of the system [25]:

$$r = \frac{k_1 K_M^2 (C_M^2 - C_W C_E / K)}{(1 + 2\sqrt{K_M C_M + K_W C_W})^4} \quad (4)$$

where  $k_1$  is reaction rate constant,  $K_M$ ,  $K_W$  and  $K$  are constants of methanol adsorption, water adsorption and chemical equilibrium, respectively,  $C_i$  is the concentration of component. Thus, by lowering water concentration  $C_W$  in ZMR, we significantly enhance the rate of dehydration.

When sweep gas was applied instead of evacuation, the rise of methanol conversion with the sweep flow rate was observed (Fig. 5). At a sweep flow rate higher than 90 ml min<sup>-1</sup> it levels off at a constant value, which corresponds to conversion obtained in the experiment with permeate evacuation. This equivalence allows us to assume that both methods can be successfully used in the ZMR regime for effective operation. Further experiments were performed with a sweep gas flow rate of 180 ml min<sup>-1</sup>.

### 3.3.2. Temperature dependence of methanol conversion

The dependence of methanol to DME conversion in the temperature range 150–250 °C at WHSV 0.9 h<sup>-1</sup> is presented in Fig. 6. At low temperatures (150–200 °C), the catalyst activity is rather low and PB operates far from thermodynamic equilibrium. Only above 200 °C the essential increase of methanol conversion was observed. Nevertheless the growth of conversion in ZMR was observed in the whole temperature range studied. This difference reveals the effect of water removal from the reaction zone. This effect is more pronounced at higher temperatures. In our case we observed a 7–10% difference in conversion below 230 °C and more than 20% difference above this temperature. Thus, when 85% of methanol conversion was reached in ZMR at 250 °C, in PB mode, the conversion of only 61% was reached at the same conditions.

The increase of reaction rate with temperature results in higher water concentration in reaction volume, leading to higher water permeation and total flux (Fig. 7). However, in the 230–250 °C temperature range, the total flux of permeate does not change. In this temperature region there is no increase of additional conversion due to ZMR application. Presumably, it is a consequence of

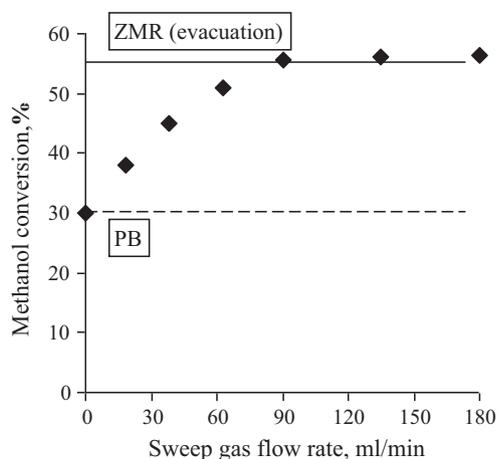


Fig. 5. The influence of sweep gas flow rate on methanol conversion in ZMR.

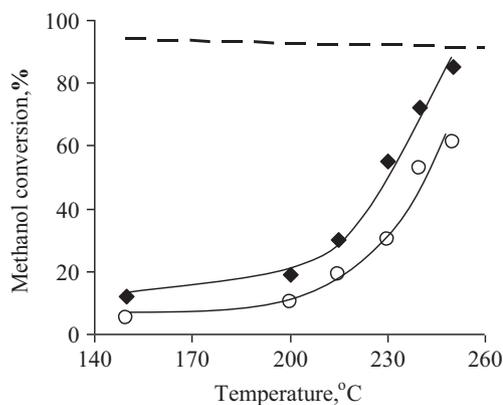


Fig. 6. Conversion of methanol into DME vs. reaction temperature in PB (○) and ZMR (◆) regimes, thermodynamic equilibrium (–).

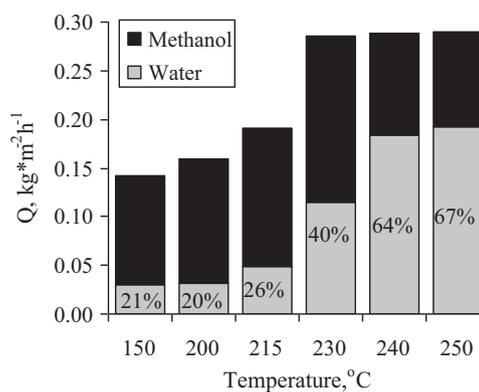


Fig. 7. Flux of permeate and its composition at different temperatures.

restricted diffusion rates of permeating species through membranes. The methanol profile along the reactor plays a significant role in permeate composition. In the upper part, the concentration of water is minimal and only methanol penetrates through membrane; along the reactor concentration of reaction products is increasing and a higher amount of water is removed by the membrane. It results in lower concentration of water in the permeate and lower total flux through membranes in comparison with water/methanol separation experiments (Fig. 3). In order to shift the formation of products before permeation, the catalyst bed is usually started before membrane region in the reactor, e.g. in [26]. This approach was not provided by the construction of our reactor so we reduced the feed flow to move the front of water closer to the top of permeation area.

As has been proved by GC analysis, DME could not pass through membranes in any operating conditions.

### 3.3.3. The impact of contact time on methanol conversion

The comparison of ZMR and PB performance as a function of contact time was studied at 230 °C and 250 °C, and WHSV was varied from 0.5 to 2.6 h<sup>-1</sup>. The dependence of methanol conversion vs. WHSV in PB and ZMR modes is presented in Table 1.

At 230 °C and high WHSV, the difference in conversion between both modes is less than 5%. The reason for such a relatively small effect of ZMR is the low residence time of water in the reactor which is enough for its effective recovery by membranes. The beneficial effect of membranes becomes appreciable at lower WHSV, when generation of water and its permeation are significant, leading to ~20% increase of methanol conversion in the ZMR regime.

**Table 1**  
Comparison of PB and ZMR modes at different conditions.

Temperature, °C	WHSV, h <sup>-1</sup>	Pressure, bar	PB mode		ZMR mode	
			Methanol conv., %	Methanol conv., %	Flux Q, kg m <sup>-2</sup> h <sup>-1</sup>	Permeate methanol content, %
230	0.5	1.0	53	77	0.32	36
	0.7	1.0	50	76	0.32	39
	0.9	1.0	41	55	0.29	58
	1.8	1.0	35	39	0.30	65
	1.8	1.7	35	34	0.66	81
	2.6	1.0	33	36	0.29	71
	2.6	1.7	33	32	0.66	80
	2.6	1.0	33	32	0.66	80
250	0.5	1.0	80	88	0.29	31
	0.7	1.0	74	85	0.32	30
	0.9	1.0	63	84	0.31	33
	1.8	1.0	49	65	0.31	49
	1.8	1.7	49	58	0.47	52
	2.6	1.0	48	62	0.30	48
	2.6	1.0	48	62	0.30	48

Higher temperature provides a higher reaction rate, and at 250 °C even in WHSV range of 1.8–2.6 h<sup>-1</sup> methanol conversion in PB is rather high and reaches ~50%. Thus, in this WHSV range water removal through membranes is also appreciable and gives an extra 14–16% conversion. Reaction rate and water permeation are two comparable factors in improving performance of the process. Lowering the WHSV in PB leads to a significant increase of methanol conversion from 48% to 80%. The same change of WHSV in ZMR results in a lower conversion increase—from 62% to 88%, which is a consequence of restricted membrane selectivity. Since a part of methanol always leaves the reactor through membranes near the reactor inlet, further increase of conversion becomes impossible, and at 0.5 h<sup>-1</sup> all water produced is passing through membranes as well as unconverted methanol. However, in a WHSV range of 0.5–1.0 h<sup>-1</sup> removal of water results in methanol conversion close to its equilibrium value.

The flux of permeate *Q* in the whole range of WHSV at both temperature regimes is around 0.3 kg m<sup>-2</sup> h<sup>-1</sup> which corresponds to the limiting step being diffusion through membranes. The content of methanol in the permeate decreases with temperature and increases with WHSV, but in all experiments it is higher than 30%. Thus the ability of methanol to pass through a NaA membrane limits total permeation flux and more pronounced increase of conversion in ZMR.

### 3.3.4. The impact of feed pressure on methanol conversion

The methanol dehydration process should be independent of feed pressure as the amount of product molecules is equal to the sum of molecules introduced into the reactor. However, higher feed pressure in methanol dehydration in ZMR may affect both permeate flux and membrane selectivity. To study this effect, 0.7 bar excess pressure was applied on the feed side of reactor (Table 1). As expected, no change in methanol conversion was observed in the PB regime. In contrast, increase of the feed pressure in ZMR results in a higher permeate flux in comparison with the results obtained at atmospheric pressure. More than a twofold increase of permeate flux was detected at 230 °C and about a 1.5-fold enhancement—at 250 °C. On the other hand, selectivity of water/methanol separation decreased with feed pressure that led to removal of methanol, which otherwise would be converted. In total, operation at higher feed pressure in ZMR demonstrated a negative effect and gave lower increase of methanol conversion.

## 4. Conclusions

Since separation of a water/methanol mixture on a NaA zeolite layer is not referred to as a size-exclusion mechanism, the separation factor significantly depends on competitive surface coverage,

determined by a feed composition, temperature and feed pressure. Synthesized zeolite NaA membranes demonstrated high separation performance and thermal resistance in relation to a water/methanol mixture at operating conditions of a methanol dehydration reaction. This allows the application of membranes in a catalytic process as water-selective walls of a reactor. More than 20% improvement of methanol conversion in ZMR over conventional PB mode was observed. An increase of temperature in the range of 150–250 °C provides more efficient operation of a membrane reactor as well as lowering of WHSV. Elevated feed pressure leads to lower selectivity of membranes and results in a decrease in ZMR efficiency. Separation selectivity of membranes and reactor design were found to be the limiting factors of the process.

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## References

- [1] E. Fontananova, E. Drioli, E. Drioli, L. Giorno, 3.05-Catalytic Membranes and Membrane Reactors, in: *Comprehensive Membrane Science and Engineering*, Elsevier, Oxford, 2010, pp. 109–133.
- [2] A.G. Dixon, Recent research in catalytic inorganic membrane reactors, *Int. J. Chem. React. Eng.* 1 (2003) 1–35.
- [3] S.-J. Kim, S. Yang, G.K. Reddy, P. Smirniotis, J. Dong, Zeolite membrane reactor for high-temperature water–gas shift reaction: effects of membrane properties and operating conditions, *Energy Fuels* 27 (2013) 4471–4480.
- [4] Y. Morigami, M. Kondo, J. Abe, H. Kita, K. Okamoto, The first large-scale pervaporation plant using tubular-type module with zeolite NaA membrane, *Sep. Purif. Technol.* 25 (2001) 251–260.
- [5] T.C. Bowen, R.D. Noble, J.L. Falconer, Fundamentals and applications of pervaporation through zeolite membranes, *J. Membr. Sci.* 245 (2004) 1–33.
- [6] M. Kondo, H. Kita, Permeation mechanism through zeolite NaA and T-type membranes for practical dehydration of organic solvents, *J. Membr. Sci.* 361 (2010) 223–231.
- [7] O. de la Iglesia, R. Mallada, M. Menendez, J. Coronas, Continuous zeolite membrane reactor for esterification of ethanol and acetic acid, *Chem. Eng. J.* 131 (2007) 35–39.
- [8] M. Pera-Titus, J. Llorens, F. Cunill, Technical and economical feasibility of zeolite NaA membrane-based reactors in liquid-phase etherification reactions, *Chem. Eng. Process. Process Intensif.* 48 (2009) 1072–1079.
- [9] W.N. Lau, K.L. Yeung, R. Martin-Aranda, Knoevenagel condensation reaction between benzaldehyde and ethyl acetoacetate in microreactor and membrane microreactor, *Microporous Mesoporous Mater.* 115 (2008) 156–163.
- [10] T.A. Semelsberger, R.L. Borup, H.L. Greene, Dimethyl ether (DME) as an alternative fuel, *J. Power Sources* 156 (2006) 497–511.

- [11] Y. Ohno, N. Inoue, T. Ogawa, M. Ono, T. Shikada, H. Hayashi, Slurry phase synthesis and utilization of dimethyl ether, *NKK Technical Rev.* 85 (2001) 23–28.
- [12] J.C. Woodhouse, Methyl ether, US Patent 2,014,408 (1935).
- [13] L.D. Brake, Dimethyl ether by catalytic dehydration of methanol, US Patent 4,595,785 (1986).
- [14] W. Kong, W. Dai, N. Li, N. Guan, S. Xiang, A one-step route to SAPO-46 using  $H_3PO_3$ -containing gel and its application as the catalyst for methanol dehydration, *J. Mol. Catal. A: Chem.* 308 (2009) 127–133.
- [15] S.-M. Kim, Y.-J. Lee, J.W. Bae, H.S. Potdar, K.-W. Jun, Synthesis and characterization of a highly active alumina catalyst for methanol dehydration to dimethyl ether, *Appl. Catal. A* 348 (2008) 113–120.
- [16] K.-W. Jun, H.-S. Lee, H.-S. Roh, S.-E. Park, Highly water-enhanced H-ZSM-5 catalysts for dehydration of methanol to dimethyl ether, *Bull. Korean Chem. Soc.* 24 (2003) 106–108.
- [17] K.-H. Lee, M.-Y. Youn, B. Sea, Preparation of hydrophilic ceramic membranes for a dehydration membrane reactor, *Desalination* 191 (2006) 296–302.
- [18] M. Farsi, A. Jahanmiri, Enhancement of DME production in an optimized membrane isothermal fixed-bed reactor, *Int. J. Chem. React. Eng.* 9 (2011) 1–18.
- [19] V.V. Volkov, E.G. Novitskii, G.A. Dibrov, P.V. Samokhin, M.A. Kipnis, A.B. Yaroslavtsev, Catalytic conversion of methanol to dimethyl ether on polymer/ceramic composite membranes, *Catal. Today* 193 (2012) 31–36.
- [20] M.A. Kipnis, P.V. Samokhin, G.N. Bondarenko, E.A. Volnina, Y.V. Kostina, O. V. Yashina, V.G. Barabanov, V.V. Kornilov, Sorption and catalytic effects upon the dehydration of methanol on perfluorinated copolymer-containing sulfo groups, *Russ. J. Phys. Chem. A* 85 (2011) 1322–1331.
- [21] K. Okamoto, H. Kita, K. Horii, K. Tanaka, M. Kondo, Zeolite NaA membrane: preparation, single-gas permeation, and pervaporation and vapor permeation of water/organic liquid mixtures, *Ind. Eng. Chem. Res.* 40 (2001) 163–175.
- [22] M.E. van Leeuwen, Derivation of Stockmayer potential parameters for polar fluids, *Fluid Phase Equilib.* 99 (1994) 1–18.
- [23] C.H. Cho, K.Y. Oh, S.K. Kim, J.G. Yeo, Y.M. Lee, Improvement in thermal stability of NaA zeolite composite membrane by control of intermediate layer structure, *J. Membr. Sci.* 366 (2011) 229–236.
- [24] C.H. Cho, K.Y. Oh, J.G. Yeo, S.K. Kim, Y.M. Lee, Synthesis, ethanol dehydration and thermal stability of NaA zeolite/alumina composite membranes with narrow non-zeolitic pores and thin intermediate layer, *J. Membr. Sci.* 364 (2010) 138–148.
- [25] G. Bercic, J. Levec, Intrinsic and global reaction rate of methanol dehydration over  $\gamma$ -alumina pellets, *Ind. Eng. Chem. Res.* 31 (1992) 1035–1040.
- [26] M.A. Salomon, J. Coronas, M. Menendez, J. Santamaria, Synthesis of MTBE in zeolite membrane reactors, *Appl. Catal. A* 200 (2000) 201–210.