



# 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  $\text{g h}^{-1}$ .

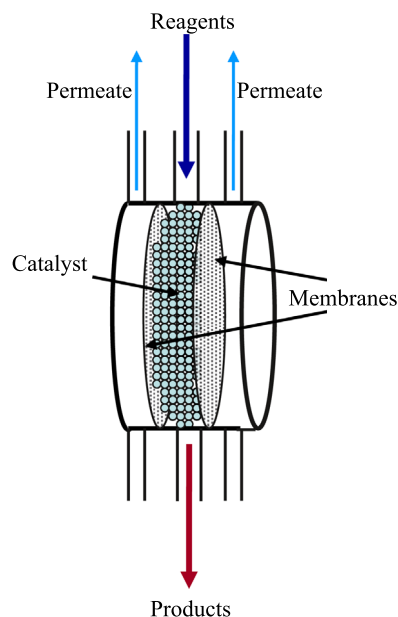


Fig. 1. Schematic diagram of MR operation.

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

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