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Asymmetry effects in membrane catalysis

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Abstract

Catalytic processes using porous ceramic where catalytic coatings on the microchannel walls are of current interest for the creation of high speed and compact membrane reactors, especially for the reactions of C_1-substrates. Nanoporous ceramic membranes with variation of pore size as a non-linear gradient can play an important role for selective mass-transfer control in membrane catalysis. This paper presents unusual results demonstrating an anisotropy in selective mass transfer in modified catalytic membranes and a related change in C_1 reaction route. To create gradient porosity, the directed formation of catalytic walls inside ceramic microchannels for C_1 reactions (e.g., methanol decomposition) is achieved by the alkoxo method. Metal-ceramic catalytic membranes with gradient porosity in the range of 2–3000 nm pore size were obtained. The proposed structural design of membranes, including the combination of catalytic coatings inside membrane channels with a top coating of a meso-porous metal oxide layer, exhibits an anisotropy in the catalytic reaction and gas permeation correlating with an improved hydrogen production. Modified high temperature ceramic membranes provide high speed methane conversion into syn-gas and light hydrocarbons at 500–650 °C, showing a good potential for the systematic study of asymmetry effects in membrane catalysis.

Keywords: Catalytic membrane reactor; Asymmetry permeation; Membrane synthesis; Methanol; Methane

1. Introduction

At present, special attention is being given to the study of heterogeneous catalytic reactions using porous membranes [1–4]. The goal is to improve the selectivity of the catalytic reactions without decreasing process productivity as well as reducing energy consumption. It is very reasonable, especially with the appearance of new membrane materials [4,5]. Traditionally, membranes are used in industrially attractive processes for the feed pre-treatment, followed by catalytic conversion or the selective recovery of the reaction products. The developments directed at the creation of microreactors combining two important aspects, namely the intensification of catalytic reactions and the simultaneous selective transport of products could be considered as novel in this field [4,5]. This kind of microreactor is the porous ceramic membrane channel modified by highly dispersed catalytic coatings. A membrane consisting of a great number of these nanochannels (10^7–10^9) can be considered as an ‘‘ensemble’’ of catalytic nanoreactors. Counterdiffusion transport in catalyst particles is replaced by unidirectional transport with the potential of intensified catalysis and increased selectivity.

The aim of the present study is the development of directed modification of ceramic membranes to create such a catalytic nanomembrane reactor system and the investigation of its permeation properties and catalytic performance in C_1 reactions. The results of methane conversion and of methanol decomposition using these catalytic membranes are presented.

2. Experimental

Oxidative methane conversion into syn-gas and light hydrocarbons was carried out using tubular ceramic membranes of ‘‘BUM’’ trademark based on titanium carbide [6] (diameter 14 mm, thickness 3 mm, geometric area 82 cm^2, average pore size ~ 4.5 μm).

Experimental runs with methane (mixture of methane/oxygen/nitrogen was varied in the range (5.8–8.6)/(4.6–2.15)/

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(89.4–89.25)) were carried out in a catalytic flow unit filtration permeability regime under a pressure drop of 3–5 bar described in ref. [5]. The feed gas mixture was fed to the inner surface of the membrane tube and gaseous products that permeated through the catalytic membrane were analyzed by on-line gas chromatography. The investigated catalytic coatings deposited inside the membrane pores were La-Ce/MgO (content catalyst was 3.6–4.4 g) and La-Ce/ZrO_2-Y_2O_3 (content catalyst was 0.6 g) systems of a cubic structure [5].

Methanol conversion was studied using TRUMEM metal-ceramic membranes (TiO_2/stainless steel) [7]. For this reaction, a $Cr_2O_3{\cdot}Al_2O_3{\cdot}ZnO$ catalytic coating formed inside the membrane channels was prepared. The catalyst composition is the same as an industrial catalyst, described in ref. [8]. For the preparation of the zinc-chromium-aluminum system, the acetylacetonates of chromium and zinc and a 60% solution of aluminum isobutylate in isobutyl alcohol were used.

Permeation measurements were carried out on set up (Fig. 1). The technique of experiment includes the transportation of gas studied from the supply [1] to the thermostating [8] diffusion cell [5]. For experiments with air, the dryer [3] is used. The temperature of the gas in the membrane diffusion cell is controlled by using the thermocouple [7] of the thermostat. Two manometers are used to control gas pressure: before and after the membrane [4,13]. Gas permeation through the membrane [6] was measured by flow meter [9]. Part of the measurements was done at TUDelft on similar equipment described in ref. [9].

Methanol conversion was studied in the membrane flow unit described in ref. [5]. Experiments were carried out in trans-membrane regime with distribution of reagents after the membrane cell as 3(retentate)/1(permeate), feeding Ar flux was 80 cm^3/min, methanol feeding was 0.1 cm^3/min, under total feed pressure 1.3–1.7 bar. The concentration of methanol vapour in Ar gas carrier was 40 mass%. A gas phase analysis was carried out by gas chromatography; the liquid phase was condensed, weighed and analyzed.

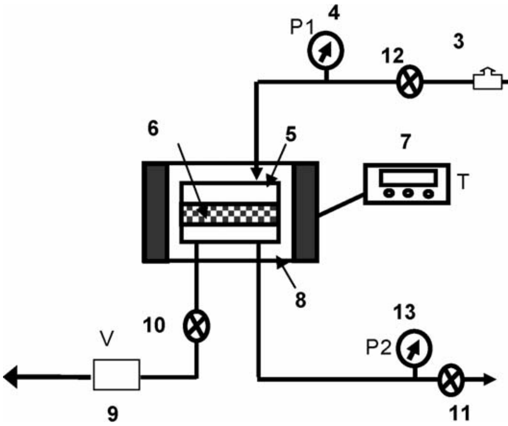

Fig. 1. The scheme of membrane diffusion cell which consists of: source of gas (1, 2), dryer (3), manometers (4, 13), diffusion cell (5), membrane (6), thermocouple (7), thermostat (8), flow meter (9) and valves (10, 11, 12).

3. Results and discussions

Earlier, it was shown for the catalytic membrane CO oxidation that with an increasing of quantity of catalyst coating at least two important parameters are increased: the effective rate reaction constant and the apparent activation energy illustrating the so-called compensation-type of catalytic reaction occurring very rarely in heterogeneous catalysis [5]. This effect seems can be a specific characteristic of membrane nanoreactors. A porous membrane as an ‘‘ensemble’’ of nanoreactors is characterized by a very short reaction time in the order of 10^{-3} s. The oxidation rate constant increases as a result of a pre-exponential factor, growing practically nine orders of magnitude. Usually, the increase of the pre-exponential factor is the evidence of an increased number of active sites and, respectively, an increase of active molecular collision frequency with the catalytically active surface.

As to methanol conversion, it was assumed that the creation of conditions for selective removal of gaseous products of this reaction could lead to an improved hydrogen yield. For this purpose, the new method of catalytic membrane preparation was developed. In this technique, the catalytic oxide system is formed inside the membrane channels, as above described, and additionally, a meso-porous layer was coated on top of the catalytic membrane. The synthesis and the structure of this single-phase oxide $P_{0.03}Ti_{0.97}O_{2\pm\delta}$ with a narrow pore size distribution in the range of 2 nm was reported earlier [10,11]. In our case, this material was obtained as a thin top layer (2 μm thickness) by spin coating. As a result, asymmetric, three-layer ceramic catalytic membranes with a pore gradient in the range of 2–3000 nm were prepared. They are: a nanoporous layer (thickness 2 μm, pore size 2 nm); a micro-porous TiO_2 layer (channels with catalytic wall coating, pore size 73 nm, thickness 20 μm) and a macroporous stainless steel layer (pore size about 3 μm, thickness 200 μm) (see Fig. 2).

The catalytic transformation of methanol into syn-gas and/or formaldehyde can occur according to reactions [12],

$$CH_3OH \Rightarrow CO + 2H_2, \quad \Delta H = 100.3\,\mathrm{kJ/mol} \tag{1}$$

$$CH_3OH \Rightarrow CH_2O + H_2, \quad \Delta H = 91.3\,\mathrm{kJ/mol} \tag{2}$$

Surprisingly, it was found that the reaction selectivity depends on the orientation of the catalytic membrane and its

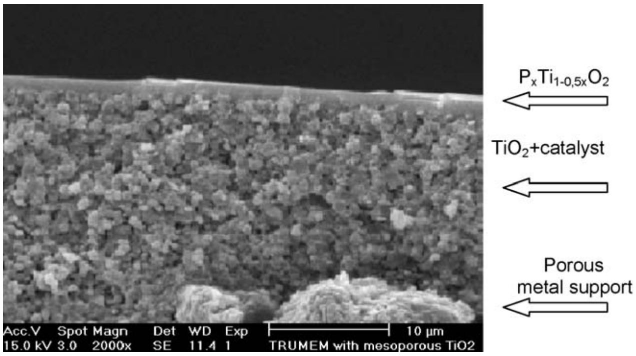

Fig. 2. SEM picture of three-layer membrane system.

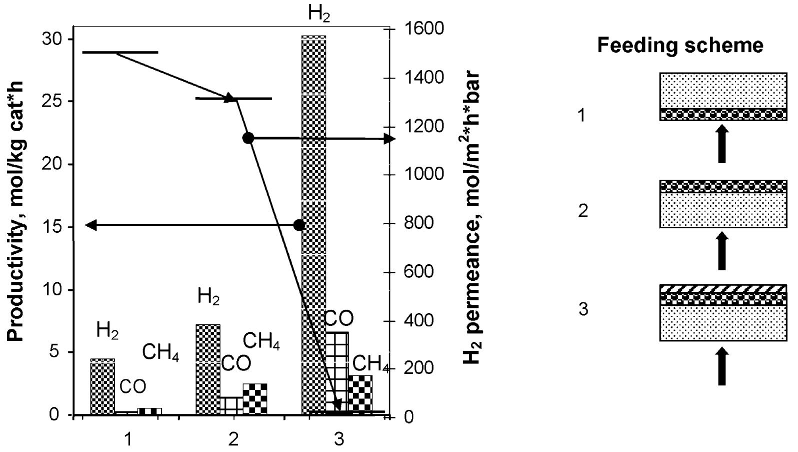

Fig. 3. Hydrogen productivity in methanol conversion process dependent on membrane porous structure and orientation ($T = 300$ °C, feeding Ar flux was 80 cm^3/min, methanol feeding is 0.1 cm^3/min, under total feed pressure 1.3–1.7 bar).

composition (Fig. 3). If methanol is fed to the side of the meso-porous selective layer, when this layer plays the role of reagent distributor only, the reaction (1) dominates if methanol is fed from the other side where the selective layer plays the role of selective removal of hydrogen, the reaction (2) dominates. With a meso-porous top layer most hydrogen is produced, while without this layer much less hydrogen is formed and even depends on the membrane orientation.

Fig. 4 shows that the composite three-layer membranes possess a permeation behavior according to Knudsen's law [10]. The trans-membrane flux is proportional to $M^{-1/2}$ (M is molar mass of gas). This dependency does not go through the origin with positive interception. It may be connected to some additional contribution of the other fluxes (surface one, activated diffusion, see Eqs. ((3)–(9)).

Surprisingly, these membranes possess an orientation-dependent permeability with respect to H_2, He, CO_2, air and CH_4. As an example, Fig. 5a and b present the permeance as a function of temperature at different trans-membrane pressures for He for two different directions; Fig. 6 demonstrates directional permeability of hydrogen. The anisotropy gas permeability effect

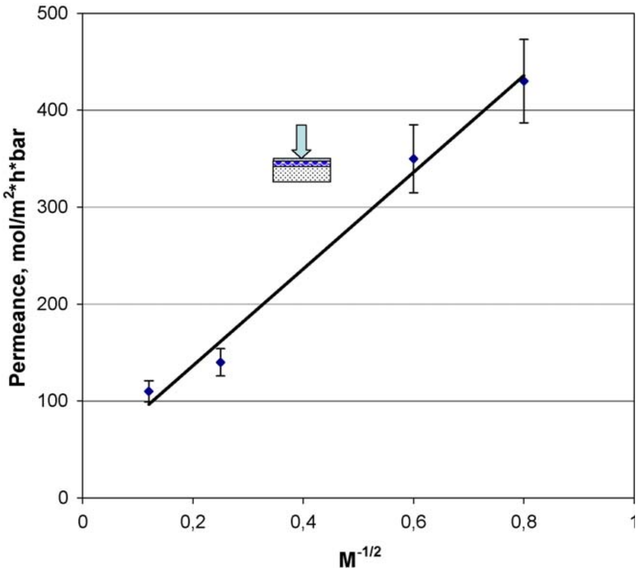

Fig. 4. Dependence of gas permeance of three-layer catalytic membrane in standard orientation on molar mass of penetrant as $M^{-1/2}$ at room temperature and pressure drop 0.8 bar.

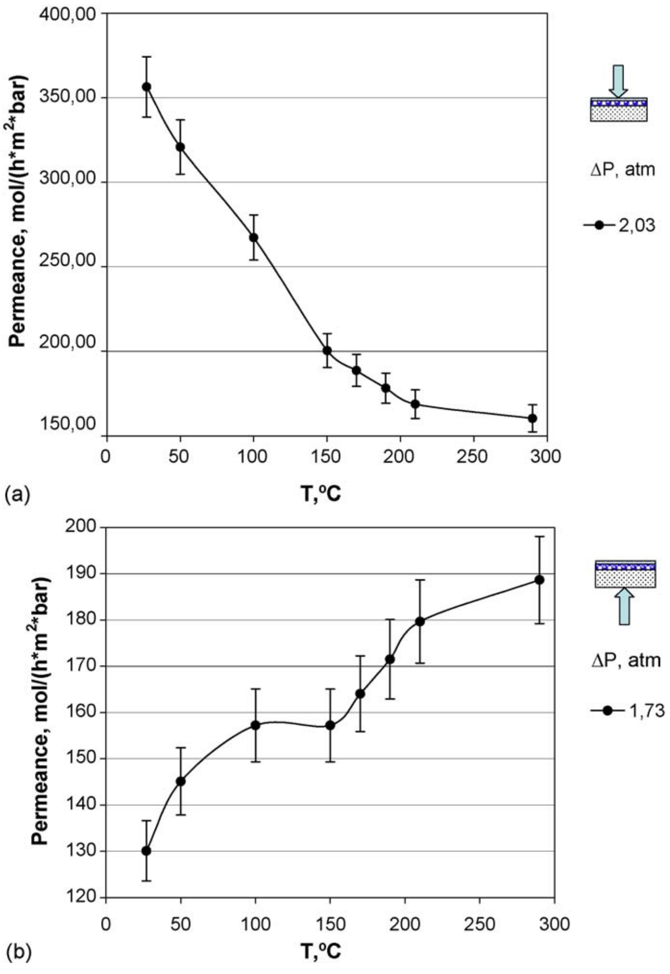

Fig. 5. Helium permeance vs. temperature for the three-layer membrane in (a) standard orientation and (b) in reversed direction at different pressure drop Δp over membrane. Key pressure drop (a) ◆ 0.54; △ 0.78; □ 1.06; × 2.03 bar. (b) ◆ 0.51; △ 0.81; □ 1.12; × 1.73 bar.

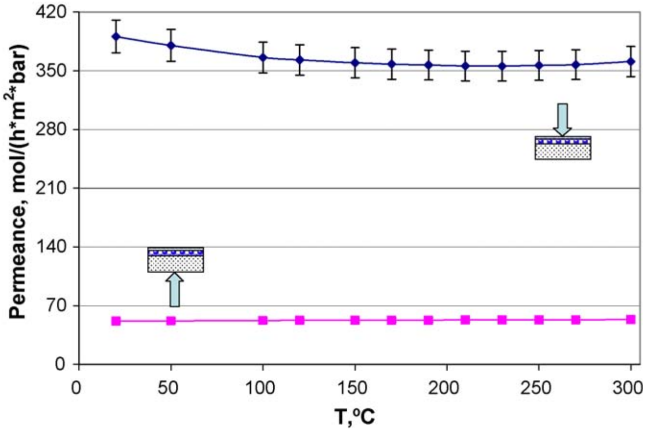

Fig. 6. Hydrogen permeance vs. temperature for the three-layer membrane in standard direction (upper line) and in reversed direction (lower line): modified ceramic membranes with gradient pore size in the range of 2–3000 nm.

for multilayer porous membranes was observed, recently [13], with gas permeance differences 3–10%. It is explained by consideration of the boundary conditions. A more significant effect was found for liquids (up to 50%) [14], which has not been explained yet.

In our case, there is substantial (a few times, Fig. 6) difference in directional permeability and temperature dependences, which is not described in the literature. We estimated that by taking into account the changing boundary conditions of pressure drop, the anisotropy in this case could not be more than 3–10%. Moreover, as can be seen from Fig. 5, there are different temperature dependencies of the gas permeance under variation of average pressure in the range of 0.5–2 bar. This unusual anisotropy phenomenon can be preliminarily explained by consideration of the possible spectrum of gas fluxes in the membrane channels. The total flux through a membrane microchannel can be the sum of the viscous one, the Knudsen flow, the surface flow and activated diffusion [9,15,16]:

$$J_{\text{total}} = J_{\text{visc}} + J_{\text{Kn}} + J_{\text{surf}} + J_{\text{act}} \tag{3}$$

where in turn the viscous flux consists of the Poiseuille and the slip flow

$$J_{\text{visc}} = J_{\text{pois}} + J_{\text{slip}}; \tag{4}$$

$$J_{\text{pois}} = -\left[\frac{a^2}{8\eta RT}\right]\beta_{\text{p}} P \frac{\mathrm{d}P}{\mathrm{d}z}; \tag{5}$$

$$J_{\text{slip}} = -\left[\frac{a}{M\nu}\right] c\beta_{\text{s}} \frac{\mathrm{d}P}{\mathrm{d}z} = \frac{3}{16} c \frac{\beta_{\text{s}}}{\beta_{\text{k}}} J_{\text{Kn}}; \tag{6}$$

where β_{p}, β_{s}, β_{k}—are dimensionless coefficients for pores of different geometry, a the average pore size and η is the viscosity (Pa s).

Knudsen flow:

$$J_{\text{Kn}} = -\frac{2a}{3}\sqrt{\frac{1}{2\pi MRT}}\beta_{\text{k}} \frac{\mathrm{d}P}{\mathrm{d}z} \tag{7}$$

Surface flow:

$$J_{\text{serf}} = g\rho q_{\text{sat}} D^{0,\text{s}} K^0 \exp\left\{\frac{-(E_a^{\text{s}} - Q)}{RT}\right\} \frac{\mathrm{d}P}{\mathrm{d}z} \tag{8}$$

Activated diffusion:

$$J_{\text{g}} = -\frac{1}{RT} g d \sqrt{\frac{8RT}{\pi M}} \exp\left\{\frac{-E_a^{\text{g}}}{RT}\right\} \frac{\mathrm{d}P}{\mathrm{d}z} \tag{9}$$

where the meanings of the parameters can be found in ref. [9]. To compare the observed differences in temperature dependencies in Fig. 5a and b, Eqs. (5)–(9) can be considered as changing of the flow spectrum. Thus, for decreasing permeance with temperature, probably, the viscous and Knudsen's fluxes dominate. For increasing permeance with temperature, the surface flow and activated diffusion may have preferable contribution. Nevertheless, it is still impossible to explain the anisotropy in gas transfer phenomena in detail. Further experimental and theoretical investigations with a systematic variation of gradient porosity are needed.

As to methane conversion, it was shown recently that in a standard flow reactor using a La-Ce/MgO membrane catalyst system that methane is selectively oxidized to light olefins C_2 and C_3 at temperature of 750–850 °C [17]. In our case, a high coke formation for La-Ce/ZrO_2-Y_2O_3 systems at 550 and 650 °C was observed at methane conversions of 60 and 70%, respectively. Coke yield represents 80%. The other 20% is syn-gas consisting of H_2 and CO in a ratio of 1/1.

The selectivity for syn-gas using the La-Ce/MgO membrane catalyst system under the same conditions was substantially higher. Fig. 7 presents the results of the reaction product composition. For conversions of 25 and 35%, the selectivity to syn-gas was 70 and 80% with an H_2/CO ratio of ≈2.5/1 and 1.5/1, respectively, and up to 5% to light hydrocarbons C_2–C_4. In this case, the selectivity to coke is not more than 5–10%.

The initial catalytic activity could be recovered by regeneration in air. The composition of partial methane

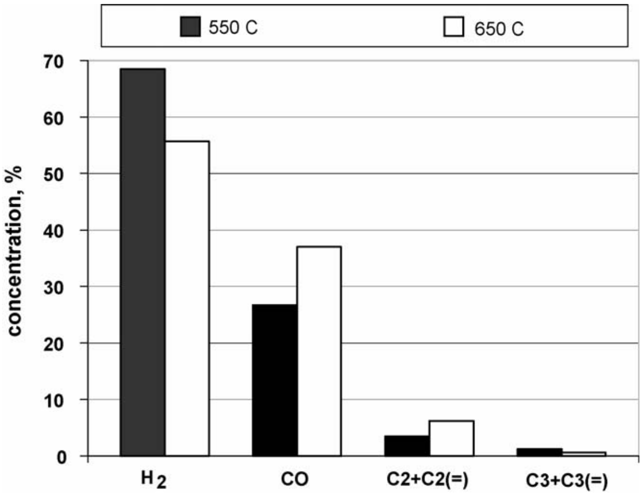

Fig. 7. Composition of gaseous reaction products of oxidative methane conversion at different temperatures over a La-Ce/MgO membrane catalyst. Key: ■ 550 °C; ☐ 650 °C.

oxidation in the membrane-catalytic reactor differs from that obtained in a standard flow reactor where main reaction products were ethylene and propylene. Besides the main reaction products (C_3, C_4, H_2 and CO), a noticeable amount of CO_2 was formed [17].

However, the methane conversion in membrane-catalytic reactor develop noticeably even at 500 °C, that is 200–400 °C, lower than in a traditional reactor. The specific productivity of H_2 creation is 3.5 volumes per one volume of ceramic membrane. It should be noted that CO_2 as a product of methane deep oxidation does not form at various relative oxygen concentrations up to O_2/CH_4–1. This result permits the assumption that a radical reaction of methane oxidation carried out without radical-chain propagations produces mainly H_2 and CO. Probably, this is one of the peculiarities of the radical catalytic oxidation reaction carried out inside nanoreactors, which are characterized by higher values of S/V (where S surface of inner walls modified by catalyst, V free volume of membrane channels). It means that, probably, radical-chain propagation is limited due to the dominant stage of chain termination occurred on the inner surface of the membrane microchannels. It can be a realistic reason for the high selectivity of methane oxidation into H_2 and CO as intermediate products of methane oxidation over membrane-catalytic systems.

We believe also that it is related to the increasing collision frequency of methane molecules with the catalytic active sites inside the membrane microchannels. The next step in our research will be directed to the creation of gradient porous ceramic membranes to investigate asymmetry effects in methane conversion.

The discovered asymmetry effects in metal-ceramic membranes with porosity gradient are extremely important for the design of gas separation inorganic membranes and catalytic membrane gas (vapour) phase reactors. This is a subject for further investigations.

4. Conclusions

In spite of being the starting phase of research in the field of structure design of nanoreactors, some preliminary conclusions can be drawn:

- The asymmetry effects in membrane catalysis for methanol decomposition provoked by the directed permeability of metal-ceramic membranes with a definite porosity gradient will stimulate the search for a new design of CMRs, Catalytic Membrane Reactors.
- The application of the sol–gel technique in membrane design allows the directed formation of complex oxide coatings providing improved catalytic and gas separation properties of ceramic membranes.
- In membrane channels modified by high dispersive catalytic coatings (“ensemble” of nanoreactors), the intensification of C_1 reactions is possible, in particular, shown by the decreased methane conversion temperature.

Techniques have been developed for the formation of hybrid meso- and micro-porous multilayer catalytic membrane systems possessing the selective transport properties of gaseous reaction products.

The phenomenon of gas permeation anisotropy is discovered in catalytic membranes with a defined gradient porosity. By the example of non-oxidative methanol conversion, it is shown that there is the possibility of the selectivity improvement of catalytic reactions in a membrane reactor using the developed structure design.

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