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Asymmetric Effects in Catalytic Membranes

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Abstract—A catalytic membrane hybrid system based on a cermet membrane with a channel size $\langle d \rangle$ of ~0.12 μm has been produced using sol–gel processing. A layer of a superfine methanol conversion catalyst with the composition $Cr_2O_3 \cdot Al_2O_3 \cdot ZnO$ has been formed on the inner surface of the channels, and a thin oxide coating of composition $P_{0.03}Ti_{0.97}O_{2 \pm \delta}$ with a homogeneous porous structure and $\langle d \rangle \sim 2$ nm has been formed on the geometric membrane surface. The methanol conversion rate and the gas permeability of the membrane depend considerably on the methanol vapor and gas (H_2, He, CO_2, Ar, CH_4) flow directions. When methanol vapor diffuses toward the mesoporous layer, the catalytic activity is one order of magnitude higher and the gas permeability coefficients are 3–8 times lower than in the case of the reverse flow of the gaseous molecules. The temperature dependence of the gas permeability taking into account the possible types of mass transfer in porous solids suggests that, when the gases move toward the mesoporous coating consisting of phosphorus-modified titanium oxide, surface flow and activated diffusion dominate, whereas the reverse gas motion is dominated by free molecular flow.

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There have been investigations aimed at creating a microreactor capable of combining a rapid catalytic reaction with selective product transport—two important factors [1, 2]. The channels of porous membranes with inner walls modified with a superfine catalytic system can serve as such a microreactor. A membrane that is a system of numerous modified channels can be considered as an "ensemble" of catalytic microreactors. We found in an earlier study that the *Trumem*™ cermet membrane [3] with inner channels modified with $Cr_2O_3 \cdot Al_2O_3 \cdot ZnO$, a catalytic oxide system similar to a commercial catalyst [4], is active in methanol dehydrogenation and hydrogenation:

$$CH_3OH \rightleftharpoons CO + 2H_2, \quad \Delta H = 100.3 \text{ kJ/mol}, \quad \text{(I)}$$

$$CH_3OH \rightleftharpoons CH_2O + H_2, \quad \Delta H = 91.3 \text{ kJ/mol}, \quad \text{(II)}$$

$$CH_3OH + H_2 \rightleftharpoons CH_4 + H_2O, \quad \Delta H = -117.6 \text{ kJ/mol}. \quad \text{(III)}$$

A high selectivity of the catalytic membrane module in dehydrogenation routes (I) and (II) is required for practical use of this process in the production of hydrogen, the most profitable energy carrier.

Here, we report the results of the development of a composite, gradient, porous, catalytic membrane system, as well as data characterizing the recently revealed permeability and catalytic activity anisotropy associated with gas flow direction in methanol conversion.

EXPERIMENTAL

A *Trumem*™ cermet membrane shaped as a disk 40 mm in diameter was employed as the inert porous base [3]. A catalytic layer of the metal oxide system $Cr_2O_3 \cdot Al_2O_3 \cdot ZnO$ was formed in the inner space of membrane channels by the sol–gel method using solutions of organic metal complex precursors [5–7]. The zinc–chromium–aluminum system was prepared from zinc and chromium acetylacetonates and a 60% aluminum isobutoxide solution in isobutyl alcohol. A thin $P_{0.03}Ti_{0.97}O_{2 \pm \delta}$ coating was produced on the geometrical surface of the cermet disk membrane using the spin-coating technique to obtain a mesoporous metal oxide membrane. This compound is characterized by a uniform pore size of ~2 nm and is described in [8]. The synthesis of the P–Ti oxide coating was performed in steps. In each step, the mother toluene solution of $Ti(OBu)_4$ etriol phosphite (0.25 cm^3) as precursors was dropped at a rate of 3 drops per second onto the surface of a rotating (2000 rpm) membrane in a fanned humid air atmosphere [8]. The system was subjected to short-term heat treatment at 500°C in Ar after gel formation on the surface of the membrane disk. After the fifth deposition, the system was heated to 500°C at a rate of 5 K/min in a muffle furnace and was held at this temperature for 6 h in an Ar atmosphere.

The catalytic activity and gas permeability of the modified membranes were studied in an apparatus equipped with high-precision pressure gauges, a chromel/alumel thermocouple for temperature mea-

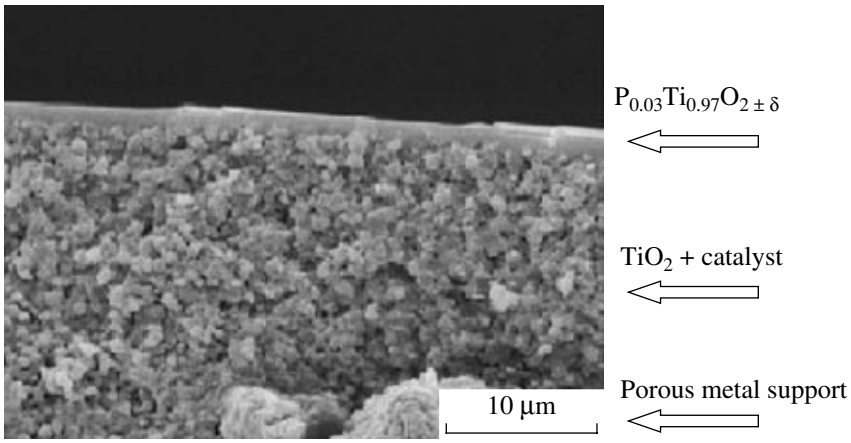


Fig. 1. Micrograph of a section of the modified catalytic membrane.

surement in the reaction zone, and automatic temperature control sensors [6]. In methanol conversion experiments, the transfer of the gaseous reagents through the catalytic membrane was carried out at a feed head pressure of 1.3–1.7 atm. Methanol vapor in the carrier gas (Ar) was passed over the membrane disk, and the gas mixture diffused through the membrane channels into the collector owing to the pressure difference. The vaporous part of the mixture that passed through the chamber of the cell and the membrane channels was condensed and weighed. The gaseous products of methanol conversion were analyzed by means of gas chromatography on a Khrom 5 chromatograph using Ar as the carrier gas and a thermal-conductivity detector. The mixture of H_2, CO, and CH_4 was separated in a 4 mm × 150 cm column packed with SKT carbon sorbent. The composition of the liquid products was determined by the GC–MS method using a Finnigan MAT 95 XL mass spectrometer (ThermoQuest, Germany) and an HP 6890+ gas chromatograph (Agilent, United States) equipped with a flow-splitting injection system. Mass spectra were obtained under the following conditions: ionizing energy 70 eV, ion source temperature 200°C, cathode current 1 mA, mass range 20–800, and scanning speed 10 mass units per second. Chromatographic analysis was performed in the isothermic mode at 50°C using a capillary column (30 m × 0.25 mm) packed with the grafted, weakly polar phase SPB-5 (poly(dimethylsiloxane) containing 5% phenyl groups, Supelco, United States) (30 m × 0.25 mm), 99.95% He (Russia) as the carrier gas, a flow split ratio of 1/30, an injector temperature of 250°C, and a mass spectrometer interface temperature of 250°C.

Gas permeability parameters were measured using the apparatus described above in the vacuum–compression mode [6]. The inlet pressure (p_{in}) was maintained in the range 1.5–2.5 atm; the outlet pressure was p_{out} = 0.2–0.5 atm. Permeability was calculated using the formula

$$Q = J/\Delta pS, \text{ mol h}^{-1}\text{m}^{-2}\text{ atm}^{-1},$$

where Q is the gas permeability of the membrane, J is the gas flow through the membrane (mol/h), $\Delta p = p_{in} - p_{out}$ is the pressure drop across the membrane (atm), and S is the geometrical surface of the membrane (m^2).

For characterization of the membrane pore structure, we employed the original dynamic desorption porosimetry method described in [6].

The coating morphology was investigated by means of scanning electron microscopy on a Philips XL30 FEG SEM microscope integrated with a Bruker-AXS D 5005 X-ray microprobe system.

RESULTS AND DISCUSSION

Figure 1 shows a micrograph of the section of the hybrid system with a layer of the mesoporous oxide $P_{0.03}Ti_{0.97}O_{2\pm\delta}$ formed on its geometrical surface. This creates a pore size gradient of 3000 to 2 nm in the membrane. Selective hydrogen elimination through the mesoporous layer during catalysis was assumed to shift the reaction equilibrium to intensive hydrogen formation. The modified membrane was found to separate gases in the free molecular flow (Knudsen) mode, in which the transmembrane flow rate is proportional to the reciprocal of the square root of the molecular weight, $M^{-1/2}$ (Figs. 2, 3). This membrane was unexpectedly found to have "directional permeability" for H_2, He, CO_2, CH_4, Ar, and some lower hydrocarbons (as is demonstrated for He in Fig. 2). Estimation of the effect of changes in the gas pressure gradient inside the gradient porous media using the procedure described in [9] demonstrated that, in our case, the permeability anisotropy must not exceed 3–10%. In fact, gas permeability coefficients differed by a factor of 3–8, depending on whether the flow vector was directed from the mesoporous layer or from the large pores. This cannot

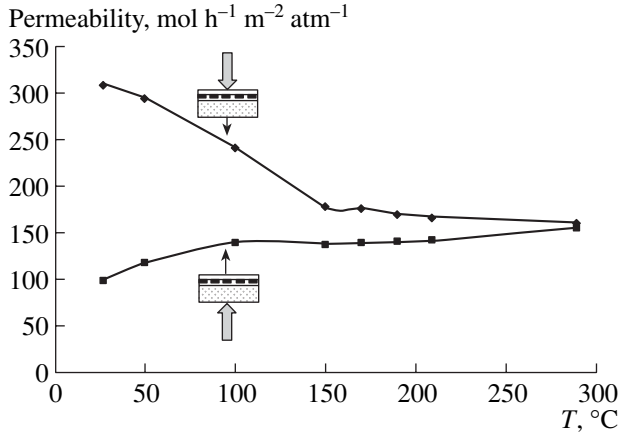


Fig. 2. Dependence of the permeability of the membrane catalyst on the helium flow direction at various temperatures.

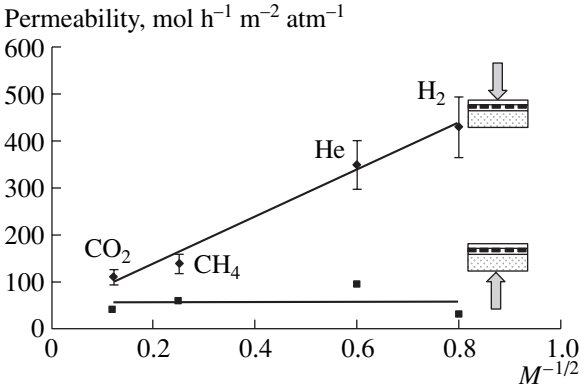


Fig. 3. Dependence of the permeability of the membrane catalyst on the flow direction for gases with different molecular weights.

be explained only by the difference between of the pressure gradients in the direct and reverse directions. Moreover, the different temperature dependences of gas permeability (Fig. 2) suggest different in gas transfer mechanisms.

A decrease in gas permeability with an increase in temperature is characteristic for viscous and free molecular flows. An ascending permeability-versus-temperature curve is characteristic of activated diffusion and, to some extent, of surface flow. The flow type in the gradient porous membranes examined is likely to depend on the flow vector. The contribution from free molecular flow dominates in the forward direction, whereas the surface flow and activated diffusion dominate in the opposite direction. Gas permeability anisotropy is noticeable even for membranes without a mesoporous $P_{0.03}Ti_{0.97}O_{2\pm\delta}$, but it is less pronounced (~10%).

It might seem appropriate to assume that an increase in the contribution from activated diffusion (the hopping transfer of molecules over the surface) to the transport of gaseous substrates in the porous material deposited on the inner walls of the membrane microchannels can significantly increase the rate of heterogeneous catalytic reactions, such as methanol conversion.

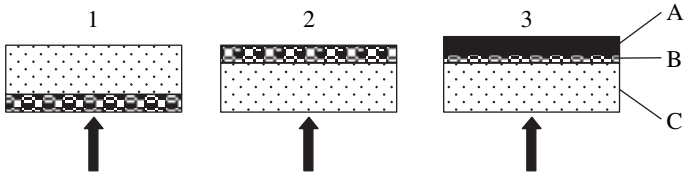
Methanol vapor fed into the catalytic membrane system is converted via all three routes, yielding H_2, CO and CH_4 as gaseous reaction products (table).

Influence of the gas (Ar + methanol) flow organization on the selectivity and hydrogen productivity of the methanol dehydrogenation reaction

Methanol feeding scheme*	Retentate/permeate**	Methanol conversion, %	Selectivity, %		H_2 productivity, mmol (g Cat)$^{-1}$ h^{-1}
			dehydrogenation	hydrogenation	
1	1	0.26	85.9	14.1	10.02
2	1	0.48	74.8	25.2	17.57
3	1	1.37	87.8	12.2	49.67
1	3	0.16	88.7	11.3	4.47
2	3	0.51	70.0	30.0	7.20
3	3	1.37	88.2	11.8	30.26

Note: T = 300°C, methanol feed rate 240 h^{-1}, and [CH_3OH] = 41 mol %.

* Methanol supply scheme:



A is the mesoporous coating, B is TiO_2 + catalyst, and C is the porous metal support.

** The ratio of the gas volume that did not pass through the membrane to the gas volume that diffused through the membrane.

Small amounts of formaldehyde were found by GC–MS among the liquid products in the permeate (the portion of the gas that had passed through the membrane). Activity and selectivity were estimated for the dehydrogenation reactions (routes (I) and (II)), which proceeded with low conversions.

The asymmetric permeability effect was found to have an effect on the catalytic properties of the modified membrane. It is clear from the table that the hydrogen productivity and dehydrogenation selectivity of the $P_{0.03}Ti_{0.97}O_{2\pm\delta}$-coated cermet membrane are higher in the case of the substrate fed from the large pore side.

On the whole, an intensification of the catalytic process in the membrane microchannels is observed when the flow is directed towards small pores.

Now we cannot provide an exhaustive explanation for the observed great effect of the gas permeability anisotropy of the composite membrane system, because the transition region of activated diffusion is inadequately explored. Our further research will be devoted to the development of a physical model of gas transport through gradient porous membrane media.

Nevertheless, the asymmetric effects discovered in catalytic membranes open up new possibilities in the design of catalytic microreactors. These can be constructed as compact integrated systems in order to combine intensive catalytic reactions with product transport.

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