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# Nanostructured phosphorus–oxide-containing composite membrane catalysts

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**Abstract**

Two types of nanostructured phosphorus–oxide-containing composite membrane catalysts were prepared by the methods of molecular layering and magnetron sputtering. The structural properties of prepared catalytic layers were measured by XRD, IR and AFM methods. The catalytic activity of composite membranes was studied in oxidative dehydrogenation of methanol in two types of membrane reactors. It was shown that application of non-permselective composite membrane catalysts could give noticeable advantages at the proper operating mode of the reactor.
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*Keywords:* Methanol oxidative dehydrogenation; Formaldehyde; V-O-P catalyst; NASICON; Membrane reactor; Membrane composite catalyst

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## 1. Introduction

For the last decade catalytic partial oxidation of alcohols and hydrocarbons has become of scientific and practical interest due to the possible application of these reactions in power source devices. Some transition metal phosphates (Cr, Mo, V, etc.) are widely known as catalysts of partial oxidation reactions [1]. In order to improve the selectivity of oxidation reactions, membrane reactors have been designed, providing a new, more efficient organization of reactant streams. The numerous studies on this issue were directed both to proper membrane and catalyst materials, as well as to the feed mode of reagents to them (e.g. [2–4]).

One of the most promising methods of membrane modification on the atomic level is that of molecular layering (ML) [5]. The ML method is based on the irreversible interaction of low-molecular reagents and functional groups of a solid substrate surface under the conditions of continuous reagent feed and removal of the formed gaseous products. For the realization of reactions in the ML process some structural conformity between the initial solid matrix surface and the reagent is necessary. There are many publications on the preparation of nanostructured catalytic systems by the ML method. Recently, we have successfully applied this method, for the first time, to the preparation of a composite membrane catalyst by the deposition of chromium–phosphorus oxide structures on the surface of a porous stainless steel sheet [6]. This membrane catalyst was used for the selective oxidation of methane to formaldehyde.

Other metal–phosphorus oxide structures which may be useful in catalytic membrane preparation are framework phosphates with $NaZr_2(PO_4)_3$, NASICON (Na SuperIonic CONductors, NZP) type construction. The crystal structure of $NaZr_2(PO_4)_3$ is based on a three-dimensional framework of corner-sharing $PO_4$-tetrahedra and $ZrO_6$-octahedra and can be best described in terms of $[Zr_2(PO_4)_3]$ structural units composed of two $ZrO_6$-octahedra linked to each other through three $PO_4$-tetrahedra [7]. A framework of NZP-type structure includes two kinds of cavities, called M1 and M2 (Fig. 1). These cavities can be populated by some cations or be vacant, and NZP structures can be considered under certain conditions as nanoporous membranes. The possibility of substitution of all the crystallographic positions of NZP structure for the whole series of ions allows their catalytic and other properties

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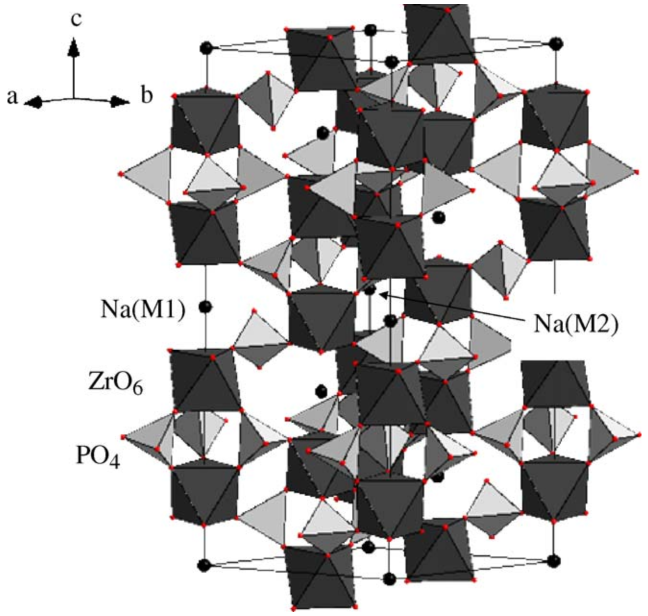

Fig. 1. Crystal structure of $NaZr_2(PO_4)_3$ NZP type phosphate.

(acidic–basic properties, conversion, selectivity, etc.) [8] to be modified. This provides a wide variety of possibilities to combine various properties of a membrane and catalyst intended for partial oxidation. Thus, the system of palladium membrane and Fe-containing NZP powder catalyst was studied earlier and was found to be effective in the methane partial oxidation to formaldehyde [9]. However, till now the formation of composite membranes with NZP structure as an active part of membrane composition is the unsolved problem of membrane catalyst preparation [10].

The purpose of this research was to develop application methods of metal–phosphorus oxide nanostructures on the surface of an inert membrane and to study the catalytic properties of such composite membranes in relation to methanol oxidative transformations. This aim was achieved first of all by using the ML method for the inorganic synthesis of vanadium–phosphorus oxide structures on the surface of an asymmetric zirconia membrane. Furthermore, for the first time we used magnetron sputtering of Fe-containing framework phosphate of the NZP type for the preparation of a composite membrane catalyst for methanol oxidative dehydrogenation.

## 2. Experimental

### 2.1. Vanadium–phosphorus oxide composite membrane preparation by ML-method

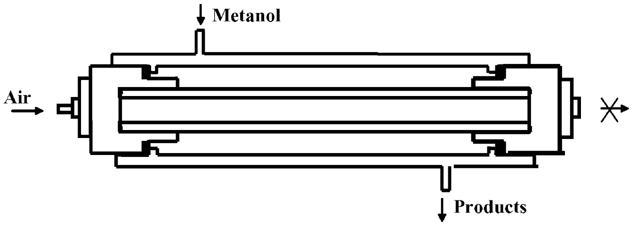

Fig. 2. Schematic diagram of tube membrane reactor.

Vanadium–phosphorus-oxide layers were synthesized on the surface of an asymmetric tubular membrane of zirconia (Schumacher, Germany). The average diameter of the wide pores of the tube was 100 nm, and that of the narrow pores was 40 nm. The synthesis was carried out in situ in the membrane reactor (Fig. 2) by the ML method at the temperature of 180 °C with alternate processing of the support by $VOCl_3$ (or $PCl_3$) vapours and water by pumping them through the pores of a zirconia membrane.

$$3(\equiv Zr{-}O{-}H) + VOCl_3 \rightarrow (\equiv Zr{-}O{-})_3VO + 3HCl \qquad (1)$$

$$(\equiv Zr{-}O{-})_3VO + PCl_3 \rightarrow (\equiv Zr{-}O{-})_3V \leftarrow OPCl_3 \qquad (2)$$

The vapor phase hydrolysis of chlorine-containing compound (2) leads to the replacement of Cl on OH-groups. The samples with one (M1) and six (M6) cycles of ML treatment were used as composite membrane catalysts.

### 2.2. NZP-layer containing composite membrane preparation

The powder of Fe-containing phosphate of an NZP type of formula $Fe_{0.33}Zr_2(PO_4)_3$ (N1) was synthesized by the sol–gel method and the formation of an NZP type structure was confirmed by methods of XRD analysis, IR-spectroscopy.

The prepared powder was pressed into a disk at pressure 3 MPa and annealed at 800 °C. The disk was used as a target for the high frequency magnetron sputtering of phosphate on a sheet (20 mm × 119 mm) of porous stainless steel with an average pore diameter of 0.1 μm. The NASICON film thickness was 1.1 μm. Fig. 3 shows the AFM pattern of the NZP membrane. The XRD analysis of the formed deposit showed its structural coincidence with that of the initial NZP powder. Thus prepared composite membrane catalyst was tested in methanol oxidative transformations in the conventional flow membrane reactor described in [11].

The main characteristics of the studied composite membrane catalysts are shown in Table 1.

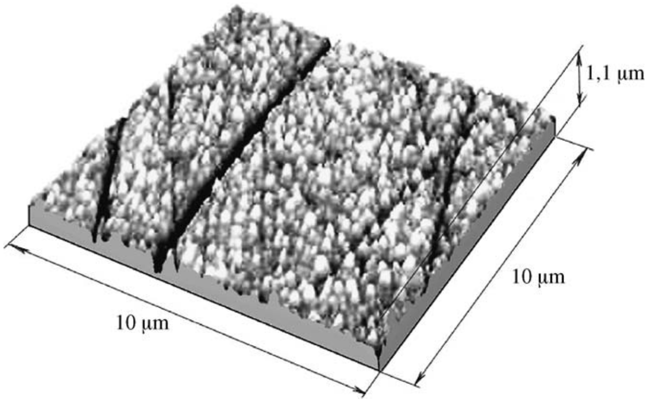

Fig. 3. AFM micrograph of composite membrane with NZP layer, deposited by high frequency magnetron sputtering.

Table 1
Characteristics of composite membrane catalysts under investigation

| | Composite membrane | | |
|---|---|---|---|
| | N1 | M1 | M6 |
| Support | Porous stainless steel sheet | Asymmetric porous zirconia tube | |
| Average pore diameter of support (nm) | 100 | 40 | |
| Active layer | $Fe_{0.33}Zr_2(PO_4)_3$ | V-O-P | |
| Geometric surface (cm$^2$) | 21 | 40.8 | |
| Active layer thickness (μm) | 1.1 | 1 layer | 6 layers |
| Specific area (m$^2$/g) | ≈25 | ≈0.1 | |
| Catalyst loading (mmol) | 0.16 | 0.025 | 0.15 |

### 2.3. Catalytic tests

Catalytic experiments on methanol oxidative dehydrogenation were carried out with both types of composite membrane. The temperature control of the reactor was accomplished by a chromel–copel thermocouple and registered by TPM temperature controller.

All the composite membranes were non-permselective. The outlet of one of the reactor zones was permanently closed. Methanol vapors in an argon flow (from a thermostat-controlled bubbler) and air were supplied separately from different sides of the membrane and the product mixture came out from one outlet tube. There were two modes of reagent introduction into the reactors: by diffusion of oxygen through the membrane to the catalyst layer (MR-O) or by diffusion of methanol through the membrane to the catalyst layer (MR-M). The initial activation procedure consisting of processing of the membrane catalyst with the reaction mixture (5% oxygen, 20% nitrogen, 5% methanol, balance nitrogen) at 50 sccm was carried out at 260 °C for 8 h.

The reaction product concentrations were measured using a Chrom Series 4 (TCD detector, Zeolite 5A column, ambient temperature, carrier gas—argon)) and LChM Series GC (TCD detectors, Porapak T and Carbon columns, 160 °C, carrier gas—helium), with the results of the analyses calculated by computer.

## 3. Results and discussion

### 3.1. Composite membranes with ML active layers

The main products of methanol oxidative dehydrogenation were formaldehyde, hydrogen, CO and $CO_2$. No dimethyl ether was found in the reaction products. The influence of O/$CH_3OH$ ratio in the overall feed of the reagents is shown in Fig. 4 for the membrane catalyst M1 at oxygen diffusion through the membrane tube to the catalytic layer (MR-O). It can be seen that the maximal formaldehyde yield was achieved at the O/$CH_3OH$ ratio between 0.5 and 1.5. It means that an excess of oxygen over stoichiometry is required for selective formaldehyde formation. The temperature dependence of a formaldehyde yield on this membrane is shown as curve 1 in Fig. 5.

Curve 2 in Fig. 5 shows the influence of temperature on the formaldehyde yield on the membrane M6 by the same feed mode of reagents. It can be seen that the activity of this catalyst is approximately twice that of catalyst M1 under other equal conditions.

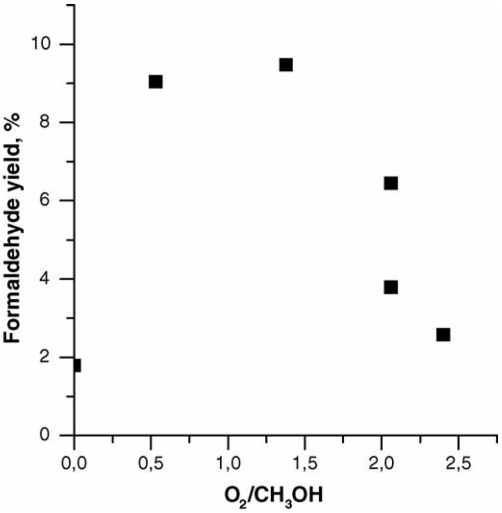

Fig. 4. Formaldehyde yield vs. O/$CH_3OH$ ratio for the membrane M1 at 260 °C and methanol concentration 5 vol%.

The change in the methanol introduction mode onto the diffusion through the membrane to the catalytic layer (MR-M)

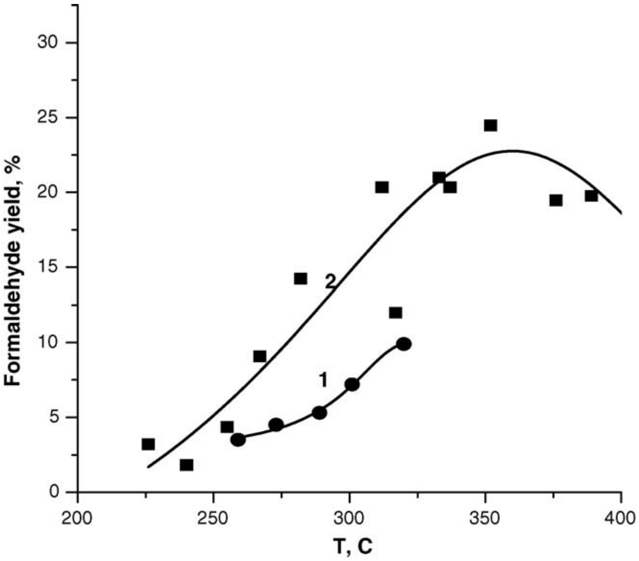

Fig. 5. Formaldehyde yield vs. temperature for the membrane catalysts M1 and M6 at methanol concentration 5 vol%, oxygen concentration 5 vol%.

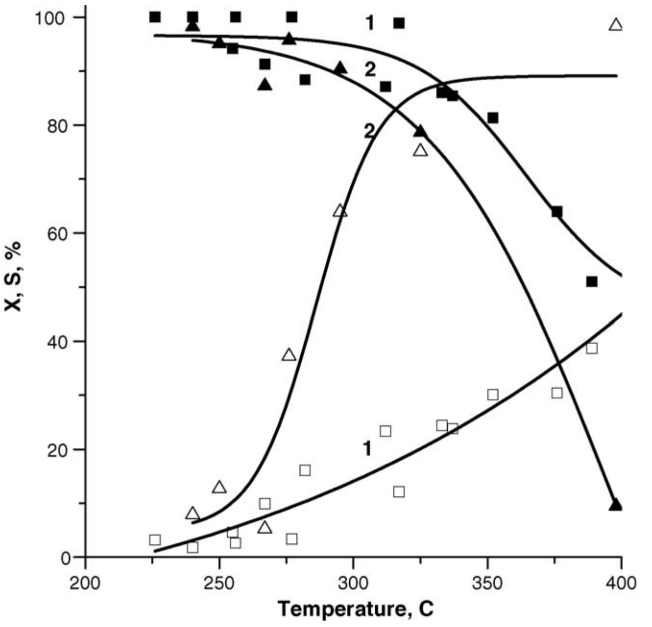

Fig. 6. Methanol conversion (open symbols) and formaldehyde formation selectivity (solid symbols) vs. temperature for membrane catalyst M6 by methanol introduction over catalytic layer (curve 1) and by diffusion through the membrane (curve 2).

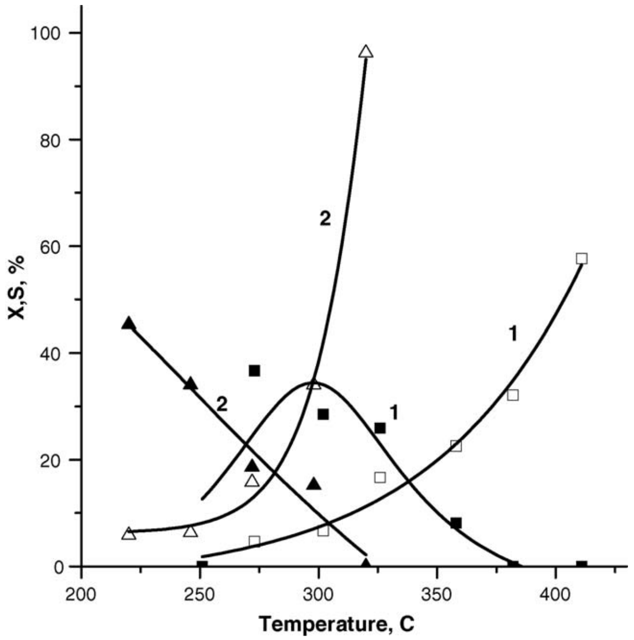

Fig. 7. Methanol conversion (open symbols) and formaldehyde formation selectivity (solid symbols) vs. temperature for membrane catalyst N1 by methanol introduction over catalytic layer (curve 1) and by diffusion through the membrane (curve 2).

increases the methanol conversion, as can be seen from a comparison of curves 1 and 2 of Fig. 6. These results differ from those of earlier published work [12] for methanol oxidative dehydrogenation over an Fe-Mo oxide catalyst in a catalytic packed-bed membrane reactor (PBMR), where the relative reactor performance was in series PBMR-O > PBMR-M. It can be attributed to the different variation of the residence time of methanol in the catalytic layer at the change of modes in reactors with the catalyst layer in the membrane pores or with a packed-bed catalyst. The complex effect of the feed mode of reactants into MR on its performance is confirmed by the results of ethylene epoxidation in a similar PBMR [13], where the ethylene oxide productivity series was PBMR-E > PBMR-O. In the latter case, as in our article, the diffusion of the reagent through the membrane is more preferable for the high yield of product of selective oxidation than oxygen diffusion through the membrane. These results clearly show the possibility of controlling the selectivity of the partial oxidation of the hydrocarbons and alcohols by changing the reactor configuration. However, for a deep analysis of vanadium–phosphorus oxide composite membrane work, it is necessary to study the reaction kinetics in a wider variation of conditions.

## 3.2. Composite membrane with NZP active layer

The methanol oxidative dehydrogenation products on NASICON composite membrane N1 were hydrogen, formaldehyde, CO, $CO_2$ and water. Membrane N1 was shown to be

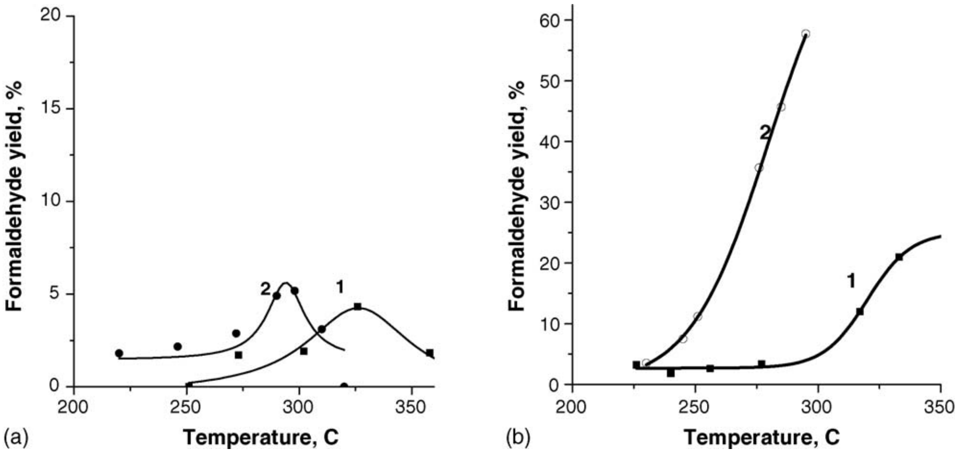

Fig. 8. Formaldehyde yield vs. temperature for membranes N1 (a) M6 (b) by methanol introduction to catalytic layer (curve 1) and by diffusion through the membrane (curve 2).

much more active at MR-M feed mode (compare the conversion curves in Fig. 7). The main products under these conditions were carbon dioxide and water, as can be seen from the low selectivity on formaldehyde in curve 2 of Fig. 7. This behaviour of the composite membrane can be attributed to the longer than optimal contact time of the methanol and reaction products with the catalyst at methanol diffusion. The formaldehyde formed can undergo further undesirable oxidation.

Fig. 8 shows the comparison of temperature dependences of a formaldehyde yield over the composite membrane catalysts N1 and M6 at different feed modes of methanol to the catalyst layer. The membrane catalyst M6 provides the highest productivity by formaldehyde at the feed mode MR-M. The vanadium–phosphorus-oxide layers are much more active and selective in the conversion of methanol to formaldehyde than an Fe-containing NZP structure at similar loading of the active components in the two membranes.

## 4. Conclusions

As a result of this work nanostructured metal–phosphorus-containing composite membrane catalysts for reactions of partial oxidation have been prepared for the first time. By the example of methanol oxidative dehydrogenation, it has been shown that the application of non-permselective composite membrane catalysts can give advantages at the selection of the proper operating mode of the reactor.

The ML method is a simple and flexible way to modify solid supports and it is rather a promising deposition method of active components during the preparation of composite membrane catalysts. The increase of the number of ML cycles of inert membrane treatment from one to six gives a significant increase in the formaldehyde yield. The highest formaldehyde yield was obtained on the membrane synthesized for six ML cycles, and at the methanol feed to the catalytic layer by diffusion through the membrane.

Preliminary experiments on the composite membrane catalyst containing an Fe-NZP phosphate as the active layer show the prospects of this membrane use in the oxidative dehydrogenation of methanol.

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