EXTENDED DISSERTATION ABSTRACT

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CONVERSION OF METHANE AND CARBON DIOXIDE ON

POROUS CATALYTIC MEMBRANES

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Foreword

This work was done under convention agreement between *A.V.TOPCHIEV Institute of Petrochemical Synthesis (TIPS-RAS)* and *Laboratoire des Sciences du Génie Chimique (UPR 6811, Nancy University).*

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The defense of the dissertation will take place on December 10, 2009 in A.V.TOPCHIEV Institute of Petrochemical Synthesis RAS.

CONTENT

Relevance of the dissertation theme.

Development of processes for obtaining valuable products from non-oil resources is one of the important petrochemical problems. Much attention is still given for development of effective processes of natural gas and other C_1-substrates conversions. Practical interest represents a process of combined methane and carbon dioxide conversion into syngas, with a purpose of rational utilization of carbon containing exhaust industrial gases. High thermodynamic stabilities of CH_4 and CO_2 molecules make the problem as a very difficult one; nevertheless these components are prospective non-oil resources for hydrocarbon and hydrogen production.

Use of membrane catalytic systems (**MCS**) in a reactor module can be an innovative solution. As a rule, membrane systems are used in catalytic processes only for low power-consuming raw materials preparation, but recently great attention is given to development of gas phase heterogeneous processes proceeding in channels of MCS, which are based on porous ceramic membranes, modified by superfine catalysts. Active surface of catalyst, formed inside channels, under relatively small area of transport pores, is characterized by high value of very important catalytic factor – S/V, which provides efficacy of heterogeneous catalytic reactions.

One of the most important petrochemical processes, which can be realized by this way, is dry methane reforming (**DMR**) into syngas.

Aim of the work.

The work purposes are the development of effective MCS for dry methane and light hydrocarbons reforming, and study of DMR dynamics in channels of catalytic membranes.

Scientific novelty.

Using alkoxy technology and metal complex precursors, preparation methods of nano-size mono- and bimetallic MCS, which contain $0.008 – 0.055\%_{mass.}$ of uniformly distributed active components on the internal side of channels, were developed for processes of dry methane and light hydrocarbons reforming into syngas in conditions of nonselective gas diffusion. It was found that average cluster size of metal oxide complexes is about 20 nm. Dynamics of DMR was studied. It was found that in channels of MCS this process is more intensive than in a traditional reactor with a fixed bed of the same catalyst. Material structures of MCS and genesis of phase compositions and oxidation levels of catalytic components during the DMR were analyzed.

Practical importance

Thermo stable high active MCS on the base of porous membranes and methods of high rate dry methane and light hydrocarbons C_1-C_4 reforming into syngas were developed. The MCS were prepared by self-propagating high-temperature synthesis (SHS) and modified by nano-size metal oxide components, which are uniformly distributed in the internal volume of membrane pores.

Using [La-Ce]-MgO-TiO$_2$/Ni-Al and Pd-Mn-TiO$_2$/Ni-Al MCS in DMR at moderate temperatures ($\leq 650°C$) syngas productivities 10500 and 7500 l/h·dm$^3_{membr.}$, respectively, with syngas compositions H$_2$/CO 0.63 – 1.25 and conversion of initial gas mix (CH$_4$/CO$_2$=1) $\approx 50\%$ were achieved.

A method of MCS using as a syngas generator for energy production in integral scheme with solid fuel cell was developed.

Approbation of the work

The principal results of the study were reported on international conferences and seminars:
- II Russian conference «Actual Problems of Petrochemistry» (Ufa, Russia, 2005),- CLUSTERS-2006 (Astrakhan, Russia, 2006),
- IIIth Russian-French Seminar (Moscow, Russia, 2006),
- XVIII Mendeleyev Congress on General and Applied Chemistry (Moscow, Russia, 2007),
- IX Conference of Young Researchers (Zvenigorod, Russia, 2008),
- PERMEA2007 (Siófok, Hungary, 2007),
- IVth Russian-French Seminar (Nancy, France, 2007), Vth Russian-French Seminar (Moscow, Russia, 2008),
- PERMEA2009 (Prague, Czech Republic, 2009),
- ICCMR9 (Lyon, France, 2009).

Publications

From the PhD results 4 articles in Russian and international journals were published, 11 abstracts of Russian and international conferences were presented and 1 Russian patent was issued.

1. LITERATURE REVIEW

1.1 Catalytic membrane reactors

Limited material and energy resources have increasingly become a challenge for future chemical production. Process intensification can contribute to the solution of this problem. From an engineering standpoint the vision of process intensification through multifunctional reactors has activated research on catalytic membrane reactors. According to the IUPAC definition, a membrane reactor is a device combining a membrane-based separation and a chemical reaction in one unit [1]. So far this engineering vision of a chemical membrane reactor could not be realized due to a lack in temperature resistant and chemically stable highly selective membranes. During the last few years, powerful inorganic membranes based on ceramics, zeolites, metals, and carbon or as a hybrid material have been developed so that the realization of a chemical membrane reactor is increasingly possible.

There are numerous concepts to classify membrane reactors [2]: following, e.g., the reactor design such as extractors, distributors, or contactors, dividing the membrane into inorganic and organic ones or porous and dense ones, using the reaction types such as oxidations, hydrogenations, isomerisations, esterifications, etc., defining inert or catalytic membrane reactors, or taking as classification principle the position of a catalyst in/near/before/behind a membrane. Different to these sophisticated concepts a simple classification of membrane reactors into only two groups will be tried as shown in Fig.1.
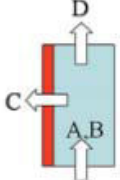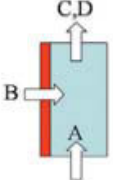
Fig.1. Classification of membrane reactors

The first group is conversion enhancement in extractor type membrane reactors operating thermodynamically near/at reaction equilibrium. To overcome the equilibrium restriction, the reaction must be sufficiently fast compared with the mass transport through the

membrane (kinetic compatibility). A special benefit can be that the removal of one of the products provides an integrated product purification thus decreasing the number of process units. Also activity improvements can be found by selectively removing reaction rate inhibitors.

The second group is selectivity enhancement in distributor/contactor type membrane reactors operating under reaction kinetics controlled conditions. The desired product is usually an intermediate in a consecutive reaction or is one of the products in a system of parallel reactions. One should note that in the case of a distributed feed along the reactor, the flow rate downstream usually increases and the residence time at the catalytic sites will be reduced.

Thus catalytic membrane reactor (CMR) involves chemical reaction and product separation that increase conversion and/or selectivity in a comparison with traditional reactors with a fixed catalyst bed.

Use CMR allows decreasing power inputs at the expense of the same conversion obtaining, as in a traditional reactor, but at lower temperature. Thus decreasing of reaction temperature reduces the contribution of side reactions, mainly carbon-producing, that decreases lifetime of catalyst. Chemical reactions in CMR are carried out with higher ecological compatibility because an increase in conversions of reagents and decrease in rates of deep oxidation reduce emissions of greenhouse gases such as carbon dioxide, methane and water steam in atmosphere [2].

1.2 Classification of inorganic membranes

The main unit of each CMR is a membrane. There is a number of membrane and membrane catalytic systems types [3].

Monolith membrane catalysts are films or light-wall tubes, which are mainly made of palladium. It is well known that palladium and its alloys are permeable only for hydrogen that makes possible to use them for hydrogen separation in dehydrogenation processes [4]. This kind of membranes are used as extractors but at the same time they also can be catalysts for dehydrogenation reaction but rate of this reaction is very low because of small specific surface of membrane [5; 6].

General requirements for use of membranes are low price, high hydrogen selectivity and permeability (in hydrogenation/dehydrogenation reactions) as well as good thermal, mechanical properties and stability [7]. For sufficient maintenance of mechanical durability a

membrane should have a thickness more than 50-100 micrometers, but as hydrogen permeability is in inverse proportion to a thickness of the membrane, in palladium membranes with the specified thickness this parameter is insufficiently high [8]. Besides, for practical use these kinds of membranes are quite expensive. They are poisoning rapidly by CO and sulfur, which present in many industrial gases.

Porous ceramic membranes are made of metal powders by self-propagating high-temperature synthesis (SHS) [9;10] and have sufficient thermo stability and chemical inertness [11]. This kind of membranes transforms to membrane catalyst by applying of ultra disperses catalytic components to the internal surface of their channels [12]. At that catalytic components can be distributed in all volume of a porous membrane, or only at one of its surfaces. Such membranes also can be rather effective in petrochemical processes, such as hydrogen production at moderate temperatures [13]. A lack of porous membranes in comparison with dense is absence of selective permeability of hydrogen what is caused by feature of their design, they have pores of micron sizes [14].

Composite membranes are prepared by applying to a porous membrane a thin layer of refractory metal and over it a layer of palladium alloy. The intermediate layer allows eliminating mutual diffusion of membrane metals and palladium alloy, and preserving high hydrogen permeability of the last one [15].

1.3 Structural design of inorganic membranes and catalytic layer formation

One of prospective methods of metal complex layer formation on different surfaces is a sol-gel process. It is a wet-chemical technique (chemical solution deposition) widely used recently in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically a metal oxide) starting from a chemical solution, which acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers. Typical precursors are metal alkoxides and metal chlorides, which undergo various forms of hydrolysis and polycondensation reactions. The formation of a metal oxide involves connecting the metal centers with oxo- (M-O-M) or hydroxo- (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution. A wide range of known heteronuclear alkoxide complexes are described by D. Bradley [16]. Thus, the sol evolves towards the formation of a gel-like diphase system containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks [17].

In the case of the colloid, the volume fraction of particles (or packing density) may be so low that a significant amount of fluid may need to be removed initially for the gel-like properties to be recognized. This can be accomplished in any number of ways. The simplest method is to allow time for sedimentation to occur, and then pour off the remaining liquid. Centrifugation can also be used to accelerate the process of phase separation.

Removal of the remaining liquid (solvent) phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification. The rate at which the solvent can be removed is ultimately determined by the distribution of porosity in the gel. The ultimate microstructure of the final component will clearly be strongly influenced by changes imposed upon the structural template during this phase of processing. Afterwards, a thermal treatment, or firing process, is often necessary in order to favour further polycondensation and enhance mechanical properties and structural stability via final sintering, densification and grain growth. One of the distinct advantages of using this methodology as opposed to the more traditional processing techniques is that densification is often achieved at a much lower temperature [18].
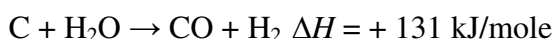
The precursor sol can be either deposited on a substrate to form a film (e.g., by dip coating or spin coating), cast into a suitable container with the desired shape (e.g., to obtain monolithic ceramics, glasses, fibers, membranes, aero gels), or used to synthesize powders (e.g., microspheres, nano-spheres). The sol-gel approach is a cheap and low-temperature technique that allows for the fine control of the product's chemical composition. Even small quantities of dopants, such as organic dyes and rare earth elements, can be introduced in the sol and end up uniformly dispersed in the final product. It can be used in ceramics processing and manufacturing as an investment casting material, or as a means of producing very thin films of metal oxides for various purposes [19].

One of the most common alkoxides of metal oxide precursors is aluminum, titanium and zirconium alkoxides. M.V. Tsodikov with colleagues had been found reactions of aluminum, titanium and zirconium alkoxides and their mixes with nickel, cobalt and iron acetylacetonates in a process of gel-formation [20]. Heat treatment of hetero metal gels has allowed obtaining single-phase metal oxide complexes at low temperatures. These metal oxide complexes are single-phase firm substitution solutions and chemical compounds. On the basis of found reactions, low-temperature methods of some single-phase metal oxide complexes formation have been developed. These oxides have great specific surface, that is essential different from analogues, obtained at high-temperatures, and causes their perspectives for use as catalysts.

1.4 Syngas production methods

Syngas is a mix of H_2 and CO, which is used as a raw stock for production of various chemical and petrochemical products (such as hydrogen, methanol, dimethyl ether, ammonia production etc.) and also for iron production [21].

Syngas for use as a fuel is most often produced by gasification of coal, biomass or municipal waste mainly by the following paths [22]:

$$C + H_2O \rightarrow CO + H_2 \quad \Delta H = + 131 \text{ kJ/mole}$$

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = - 393.5 \text{ kJ/mole}$$

$$CO_2 + C \rightarrow 2CO \qquad \Delta H = +172.5 \text{ kJ/mole}$$

When used as an intermediate in the large-scale, industrial synthesis of hydrogen (principally used in the production of ammonia), it is also produced from natural gas (via the high endothermic steam reforming reaction) as follows:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H = +206 \text{ kJ/mole}$$
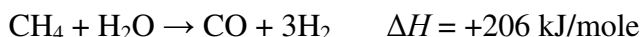
In order to produce more hydrogen from this mixture, more steam is added and the water gas shift reaction is carried out:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -41.2 \text{ kJ/mole}$$
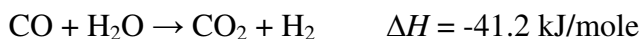
But the hydrogen must be separated from the CO_2 to be able to use it.

This is the most common but also very expensive method of syngas production, which needs much energy. The cost of industrial installation of steam reforming of methane is about 60% of total cost of natural gas to liquid fuels conversion factory [23].

Another industrial method of syngas production is a partial oxidation of methane (POM):

$$CH_4 + 1/2O_2 = CO + 2H_2 \qquad \Delta H = -35.6 \text{ kJ/mole}$$

Efficiency of the process decreases because of nitrogen and nitrogen oxides content in a product. It is also important to notice that the chain-radical mechanism of the reaction complicates the process control and consequently its realization in a traditional flowing reactor because of serious risk of explosion.

A special place among all known syngas production methods takes plasma-chemical oxidation of hydrocarbons with water steam. An advantage of this process is a combination of non-equilibrium high-voltage catalytic methane oxidation by mix of air with water steam at atmospheric pressure that essentially increases methane conversion into H_2 and CO. An optimal temperature of this process is about 3200K [24].

The greatest disadvantages of plasma-chemical oxidation are difficulties in industrial realization of this method due to non-typical construction of reactor. For the moment this method is on laboratory testing stage [25].

One of the developing methods of syngas production is a process, based on use of dense oxygen-conductive membranes with mixed ionic conductivity, in a combination with selective oxidation of methane into syngas in the same reactor. However, this technology imposes constraints on its application. Membranes must be high oxygen-conductive (~ 10 + $sm^3O_2/sm^2 \cdot min$) in the temperature range of 700 – 1000°C as well as durable, chemical and phase stable in conditions of high gradient of oxygen chemical potential (pure methane on the one hand, membranes and air – on the other hand). Also they must be stainless and steady against chemical poisons; they must be compatible for catalyst application. At present time there are no any membrane materials with all satisfactory properties [26].

An alternative method of syngas production is based on a combined conversion of methane and carbon dioxide (dry methane reforming, further DMR). However, for the moment there is no industrial realization of DMR firstly because this process is high endothermic, that is demanding high power inputs, secondly, the most active well known nickel catalyst is low stable and during the reaction cokes rapidly. Within the limits of a carbon formation problem, searches of new catalysts are continuing. As to reduction of power inputs, the decision of this problem can be various combinations of DMR with exothermic reactions, usually with partial methane oxidation or with full oxidation of methane into CO_2 and H_2O, or realization of the process on membrane catalytic systems based on porous ceramic membranes, modified by nano-structural catalysts.

$$CH_4 + CO_2 = 2CO + 2H_2 \qquad \Delta H = +247 \text{ kJ/mole}$$
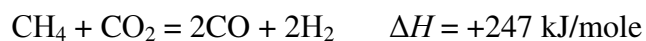
The main advantage of this approach is shifting of process temperatures to the moderate area (500-650°C) at the expense of improved heat and mass transfer in membrane channels. Varying basic technological parameters in a wide range, it is possible to obtain syngas with different H_2/CO ratios that allows fine adjusting for needs of a consumer [27].

1.5 Catalysts for dry methane reforming process

The most active in DMR are applied nickel catalysts, but they have very big disadvantage – deactivation during the process due to carbon formation. There are different methods to control this problem. So, in the SPARG process (TOPSOE), carbon inhibits by

sulfur passivation [28]. It is considered that sulfur blocks formation of big carbon ensembles and thus inhibits carbon formation stronger, than dry methane conversion.

Catalysts, where nickel is applied to basic carriers, are less exposed to carbon deposition. Thus, if Ni/Al_2O_3 catalyst is very active in DMR on the initial stage, Ni/MgO, Ni/CaO, Ni/MnO, Ni/ZrO_2 catalysts have stable activity for a long period of time. It was noted that carbon formation inhibits if metal is applied to carrier with high Louis basicity [29; 30]. On such oxides as CaO, MgO and TiO_2 adsorbed carbon dioxide reacts with carbon by reverse Boudoir reaction:

$$C + CO_3^{2-} = 2CO + O^{2-}$$
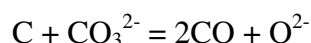
There are also basic additions to Al_2O_3 carriers. Probably, formation of non-stable carbonates facilitates its reaction with carbon.

Differences between applied catalysts and catalytic systems, that are chemical compounds, were found for $Ni+Al_2O_3$. Such catalyst is more active and stable than applied Ni catalyst [31].

According to [32] high porosity of Ni-catalysts on Al_2O_3, SiO_2 and MgO promotes its catalytic activity.

Ni/MgO ($Ni:MgO = 1:1$) catalyst with additions of Cr_2O_3 and La_2O_3 [33]. It was found that addition of these components increases stability of catalyst to carbon formation. Such promotion increases oxidation level of nickel that decreases tendency of methane dehydrogenation into carbon.

Platinum metals in DMR are more active than Fe, Co, Ni, and they are less exposed to carbon formation due to less carbon solubility in them. Platinum metals have only one great disadvantage – very high price [34].

In Gubkin Russian State University of Oil and Gas was found that catalytic system on the base of La-Ce/MgO is high active in processes of selective methane conversion into syngas and light hydrocarbons C_2 and C_3 in a flow bed reactor at 750-850°C [35; 36].

Summarizing results, it has to be ascertained that nickel is more preferable catalytic component for DMR. Research efforts are directed to decrease of carbon formation on the nickel surface. Increasing of nickel dispersion and use of basic carriers for catalyst application or metal-promoters, which decrease carbon solubility, can be a way out. From known applied components practical interest represent high active La-Ce catalysts and platinum metals.

2. EXPERIMENTAL

2.1 Experimental methods

In this study original tube porous ceramic membranes, prepared by self-propagating high-temperature synthesis (SHS) [37] from high dispersive metal powders, were used (Fig.2).
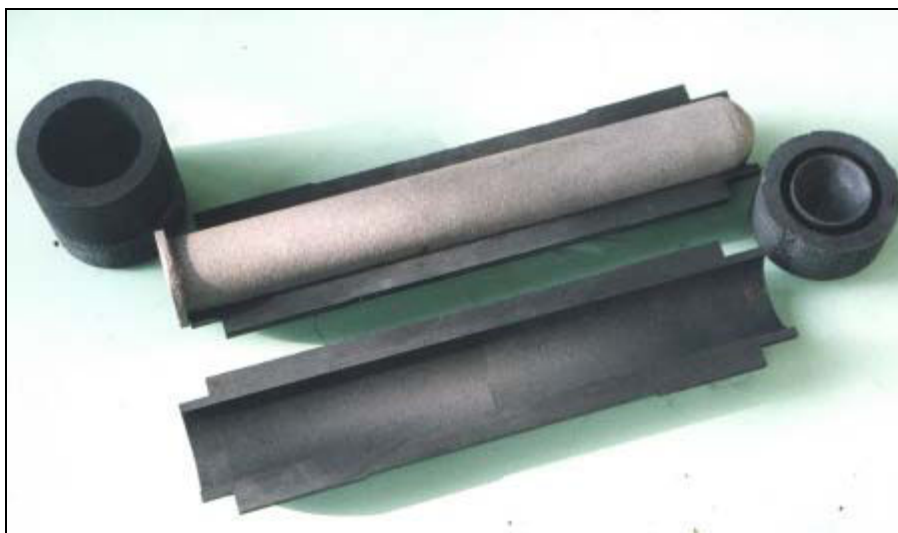

Fig.2. Original tube porous ceramic membrane.

Altogether 4 types of membranes were studied: Ni-Al-FeC, Ni-Al, Ni-Al-Co and Ni-Ti. Geometrical sizes of samples are: length - 127 mm; outside diameter - 16 mm; wall thickness - 4 mm, pores/cm^2 10^8 — 1 cm^2.

Membrane catalytic systems were prepared by application of active components to ceramic membranes [12]. Modification of membranes inner surface by original superfine metal oxide catalysts was done by sol-gel method (Fig.3).
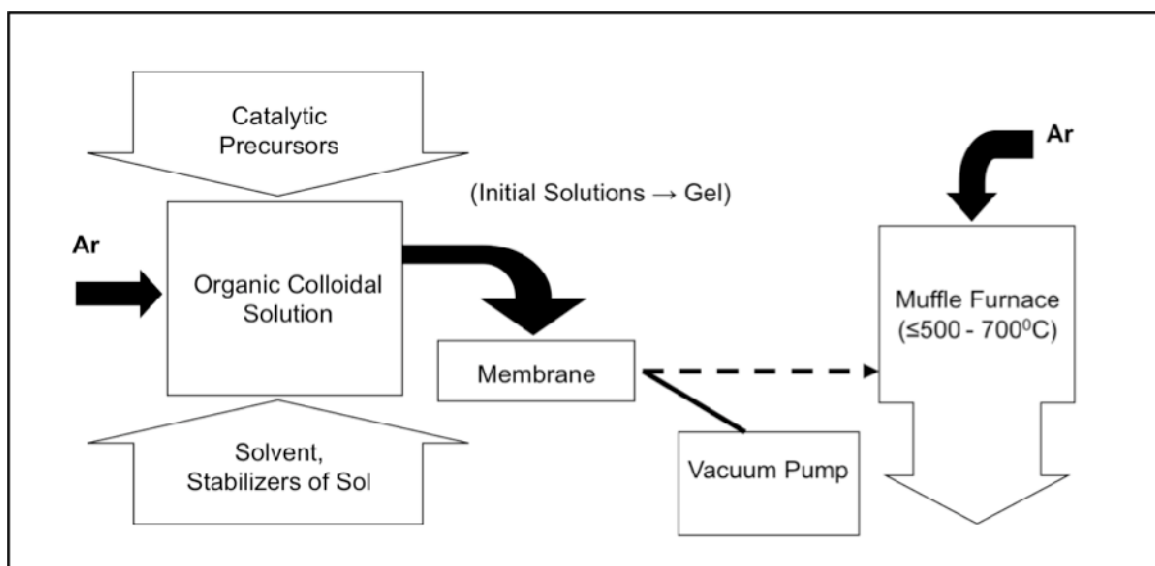
Fig.3. Scheme of catalytic layer formation by sol-gel method.

Initial solutions of metal oxide precursors were pumped through the membrane on the laboratory stand, connected to a vacuum pump. Then a membrane was heated in a flow of dewy heated air, dried in a vacuum and heat-treated. At first internal surface of membrane was coated by a buffer layer of TiO_2, obtained from a toluene solution of n-butoxytitanium and heat-treated at 300, 500 and 700°C.

Data about applied active components and their quantities are given in the Table 1.

Table 1. Active components and theirs quantities.

Active components		$\%_{mass}$, of membrane mass	
1st	2nd	1st	2nd
La	Ce	0.0200	0.0350
Pd		0.0230	
Mn		0.0230	
Pd	Mn	0.0150	0.0080
Pd	Co	0.0140	0.0070
Pd	Zn	0.0300	0.0150
Re	W	0.0530	0.0530
Au	Ni	0.0029	0.0009

Membrane catalytic stand (Fig.4) consisted of a gas-cylinder for an initial gas mix (1), a reducer (2), a flow rate regulator (3), a preheater (4), a manometer (5), two thermocouples (6,7), an original membrane reactor with a heater (8), a collector (9), a valve (10), a CO-analyzer (11), a gas-chromatograph (12), a digitizer (13), a PC (14) and an armature.
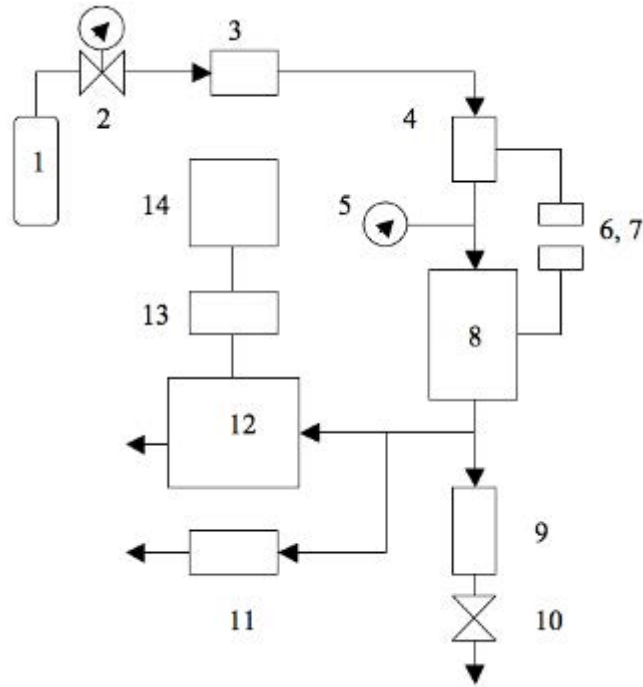
Fig.4. Membrane catalytic stand.

Scheme of an original membrane reactor is presented in the Fig.5.

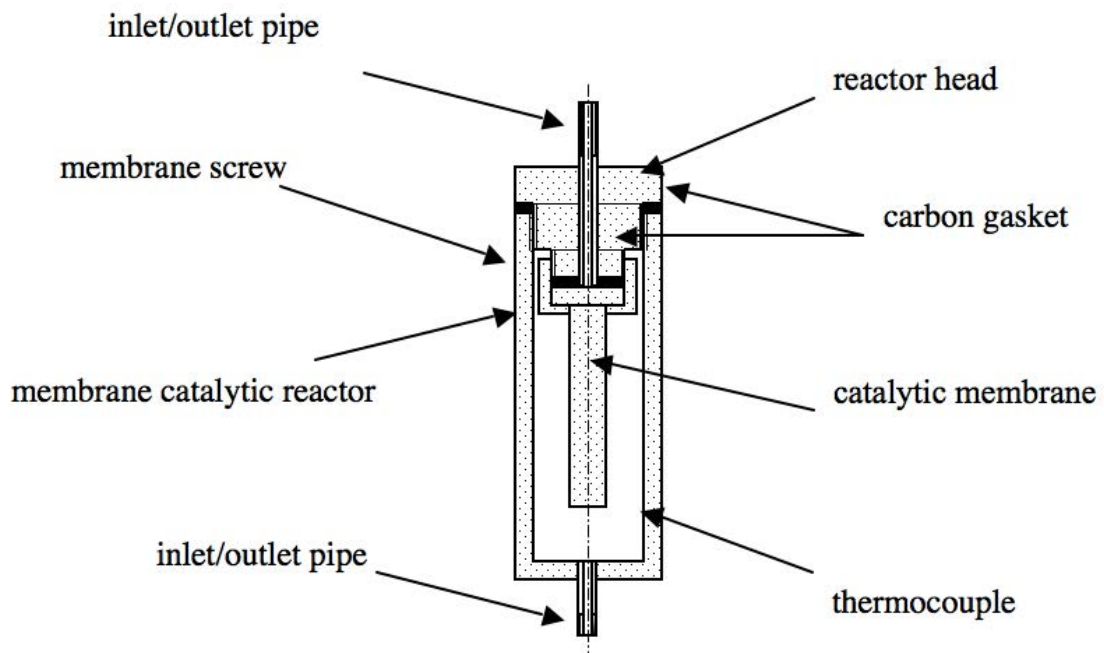Fig.5. Membrane catalytic reactor.

Dry reforming of methane and light hydrocarbons was studied in the following conditions: temperature — $\leq 800°C$, inlet pressure — up to 5 atm, outlet pressure — 1 atm, flow rate of an initial gas mix $CH_4/CO_2=1$ (in DMR) – up to 400 l/h. Initial gas mix ran on an

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external side of the membrane. Before each experiment membrane catalytic stand was prepared in accordance with order.

Gaseous products were analyzed on-line by gas chromatography using «CHROM5» device, equipped by catharometer. UHP Argon (30 ml/min) was used as a gas-carrier, activated carbon «SKT», treated by water vapor for the reason of micro pores adsorption decrease, was used as an adsorbent (chromatographic column size — 1m x 3mm; particle sizes — 0.2-0.3 mm). Quantitative analyze was done by method of absolute calibration using «ECOCHROM» software (Russia).

Concentration of CO was analyzed by Riken Keiki RI-550A device. The absolute accuracy of device is ± 0.01% in a range up to 2% and ± 0.05% in a range up to 7%.

Permeability of membrane catalytic systems was studied using the same laboratory stand as presented in the Fig.4. at room temperature. Air was used as a model gas.

Dynamics of DMR on membrane catalytic systems was studied on the thermo gravimetric cell (Fig.6) with use of «SETSYS Evolution» thermo analytic device, equipped with balance and mass-spectrometer.
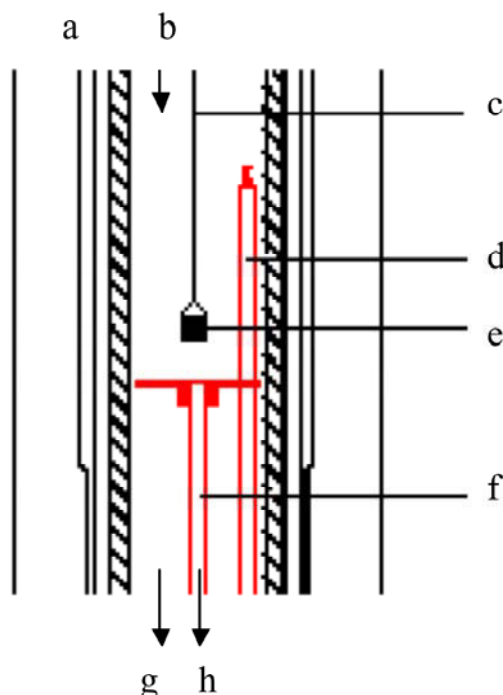

Fig.6. Scheme of a thermo gravimetric cell.
(a) furnace, (b) inlet pipe, (c) quartz thread, (d) thermocouple, (e) sample batch (f), aluminum capillary for sampling, (g) outlet pipe, (h) inlet pipe of mass-spectrometer.

Samples were heated in a flow of $CH_4/CO_2=1$ (20 ml/min) in a temperature range 30-700°C with rate 10°C/min during one hour and a half.

Structures of membrane catalytic systems were analyzed by helium pycnometry, mercury porosimetry, nitrogen sorbtiometry (BET), SEM+EDX, TEM, XRD, TPR and XAFS.

Density of membrane materials was measured by helium pycnometer AccuPyc 1330.

Pore structure was studied using Micromeritics AutoPore IV mercury porosimeter.

Specific surface of membrane catalytic systems was studied by BET method on SORPTOMATIC 1990 device.

Morphology and elemental composition of membrane surface was studied by SEM-EDX on JEOL JSM-T330A microscope.

Material fine structure was studied by TOPCON EM-002B transmission electron microscope with LaB_6 electron source.

Crystalline structure was studied by XRD on Bruker D8 ADVANCE device with $Cu_{K\alpha}$ radiation in 2Θ angles range 10-100°. Reflexes intensities were identified by Diffrac Plus EVA software.

Thermo programming reduction (TPR) was studied on original installation, equipped by chromatograph Schimadzu GC-17A. Well-milled samples (50-120 mg) were loaded into hermetic U-shaped quartz reactor and heated in a range of temperatures 25-900°C (15 deg/min) with automatic registration of hydrogen concentration. The experimental data was analyzed by original device software.

2.2 Calculations

Mass balance:

$$M_{CH_4}-M'_{CH_4}+\sum M_{CO2}=\sum M_i+\delta,$$

M_i - mass of incoming methane (g);

M'_{CH_4} - mass of non-converted methane (g);

$\sum M_{CO2}$ - mass of incoming CO_2 (g);

$\sum M_i$ - lump sum mass of gas products (g);

δ - unbalance, concerned with water and carbon formation.

Conversion of reagents:

$$X_i = \frac{M_i - M_i^{'}}{M_i} \cdot 100$$

Quantity of reagents and products were calculated on the basis of their concentrations and molecular weights, flow rate of initial gas mixture and duration of an experiment. In the case of dry methane reforming at comparable concentrations of CH_4 and CO_2 it is necessary to do an item balance.

Quantity of reaction products:

$$M\copyright_i = \frac{C_i \cdot \omega \cdot \tau \cdot m_i}{100 \cdot 22.4}, \qquad [g]$$

C_i – concentration of a product %vol;

ω – flow rate of products, l/h;

τ – duration of an experiment, h;

m_i - molecular weight of a product, g/mol.

Process productivity:

$$\rho_i = \frac{C_i \cdot \omega}{100 \cdot V_{membrane}}, \qquad \left[\frac{l}{dm^3 \cdot h} \right],$$

$V_{membrane}$ – volume of a membrane, dm^3.

Permeability

$$Q = J_{out.}/(S_{av.\ flank\ surface} \cdot \Delta P), \ l/(h \cdot m^2 \cdot atm)$$

$J_{out.}$ – outlet gas flow, l/h;

$S_{av.\ flank\ surface}$ – average flank surface of a membrane, m^2;

ΔP - pressure drop, atm.

Coefficient of permeability

$$P = Q \cdot h_{membr.}, \ l \cdot sm/(h \cdot m^2 \cdot atm)$$

Q – permeability, $l/(h \cdot m^2 \cdot atm)$;

$h_{membr.}$ – wall thickness of membrane, sm.

3. RESULTS AND DISCUSSION

3.1 Study of catalytic activity and selectivity of original membrane catalytic systems

3.1.1 Dry methane reforming

As it has been already said above, in DMR process several types of ceramic membranes were tested, namely Ni-Al-FeC, Ni-Al and Ni-Ti.

It was found that Ni-Ti membrane is the most active in DMR process but this kind of material is not durable. The reason of it is that titanium absorbs hydrogen at high temperatures with formation of fragile hydrides. It also has to be noted that obtained syngas is rich of carbon monoxide.

The most durable was Ni-Al-Fe membrane but its catalytic activity in DMR was very low.

Ni-Al-Co has no satisfactory adhesion properties and modification of this membrane was difficult. Moreover, Ni-Al-Co membrane, modified by La-Ce catalyst, had catalytic activity comparable with the virgin one (Table.2).

Ni-Al composition was chosen for nano-size metal oxide catalysts application as the most appropriate by durability, catalytic activity and adhesion properties.

It was found that [La-Ce]-MgO-TiO$_2$/Ni-Al is the most active and [Pd-Mn]-TiO$_2$/Ni-Al is the most selective membrane catalytic system (Table 2).

Table 2. DMR on different membrane catalytic systems (T=600°C, W$_{feed}$=40 l/h, CH$_4$/CO$_2$=1)

№	Carrier	Catalyst	ρ(syngas), l/h·dm^3$_{membr.}$	H$_2$/CO	X, %$_{vol.}$	
					CH$_4$	CO$_2$
1	Ni-Al-FeC	—	176	0.07	9.0	3.3
2	Ni-Al(granules)	La-Ce	249	0.66	10.3	6.8
3	Ni-Al	—	327	0.10	13.5	1.4
4	Ni-Al-Co	—	344	0.36	13.9	6.2
5	Ni-Al-Co	La-Ce	516	0.42	20.9	9.3
6	Ni-Al	Pd-Co	708	0.2	25.3	9.9
7	Ni-Al	Re-W	1084	0.68	23.1	19
8	Ni-Al	Mn	1660	1.62	31.0	5.4
9	Ni-Al	Pd-Zn	1790	0.96	34.3	34.3
10	Ni-Al	Pd	2050	1.41	45.5	29.4
11	Ni-Ti	—	2171	0.55	43.3	29.8
12	Ni-Al	Pd-Mn	3344	1.25	46.8	31.5
13	Ni-Al	La-Ce	3780	0.63	51.2	26.1

It was found that [La-Ce]-MgO-TiO$_2$/Ni-Al and [Pd-Mn]-TiO$_2$/Ni-Al systems are more stable against carbon formation on the catalyst surface than monometallic. The highest syngas productivities for [La-Ce]-MgO-TiO$_2$/Ni-Al and [Pd-Mn]-TiO$_2$/Ni-Al are correspondingly 10500 и 7500 l/h·dm$^3_{membr.}$ (Fig.7), it also has to be noted that syngas selectivity is higher on Pd-containing system (Table 2).
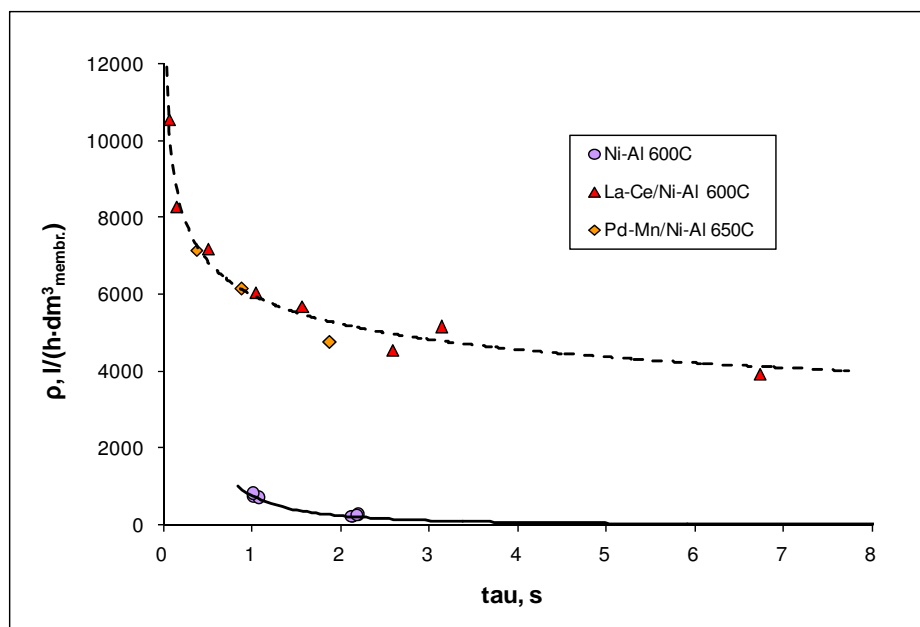

Fig.7. Syngas productivity *vs.* time residence on [La-Ce]-MgO-TiO$_2$/Ni-Al and [Pd-Mn]-TiO$_2$/Ni-Al in compare with Ni-Al.

A non-additive effect of activity increase was found for mixture of Pd and Mn catalytic components (Fig.8).
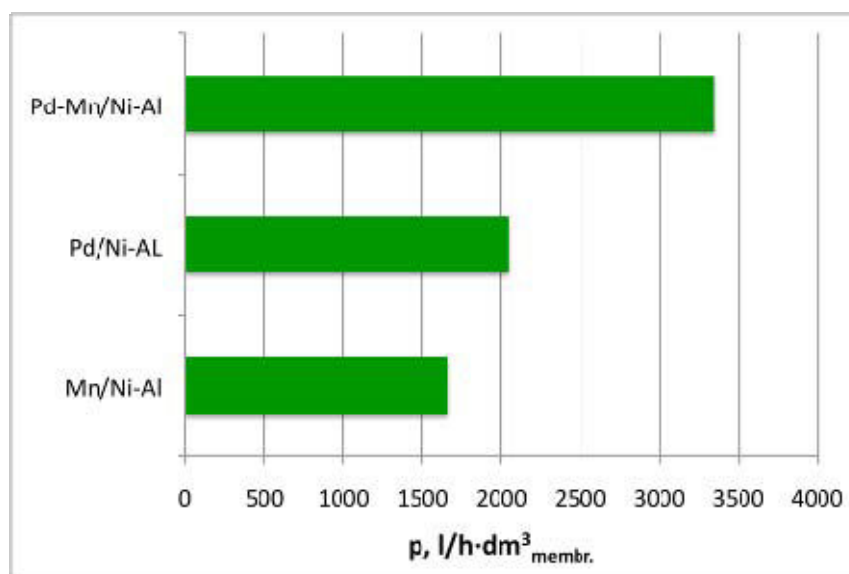
Fig.8. Syngas productivity *vs.* catalyst composition. Non-additive effect of activity increase.

It was found that conversion of carbon dioxide is essentially lower than conversion of methane on [La-Ce]-MgO-TiO$_2$/Ni-Al membrane catalytic system in the whole range of studied temperatures (Fig.9).
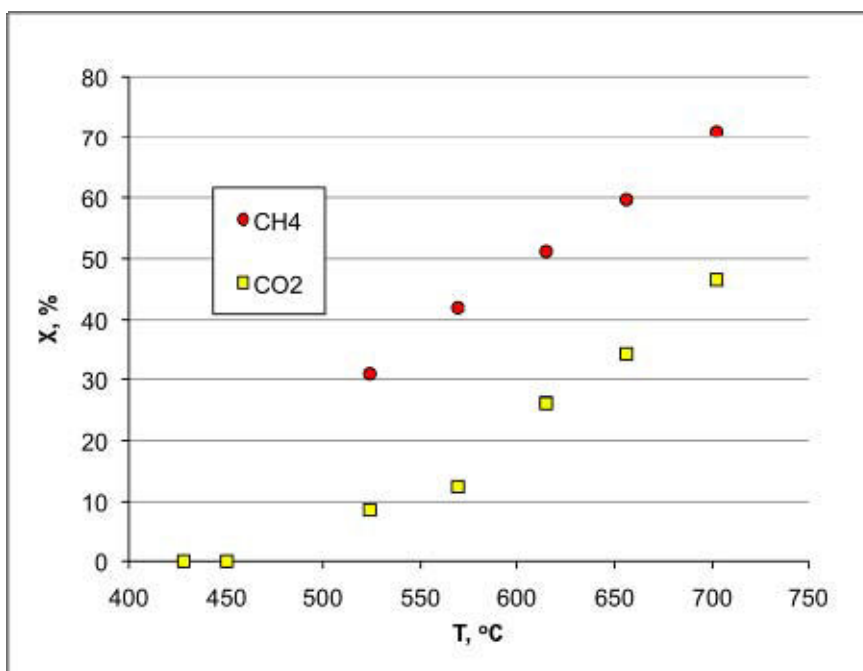
Fig.9. Conversions of methane and carbon dioxide *vs.* temperature on
[La-Ce]-MgO-TiO$_2$/Ni-Al system (W$_{feed}$=40 l/h).

On [Pd-Mn]-TiO$_2$/Ni-Al conversion of CO$_2$ is closer to conversion of methane due to higher selectivity of catalyst (Fig.10).
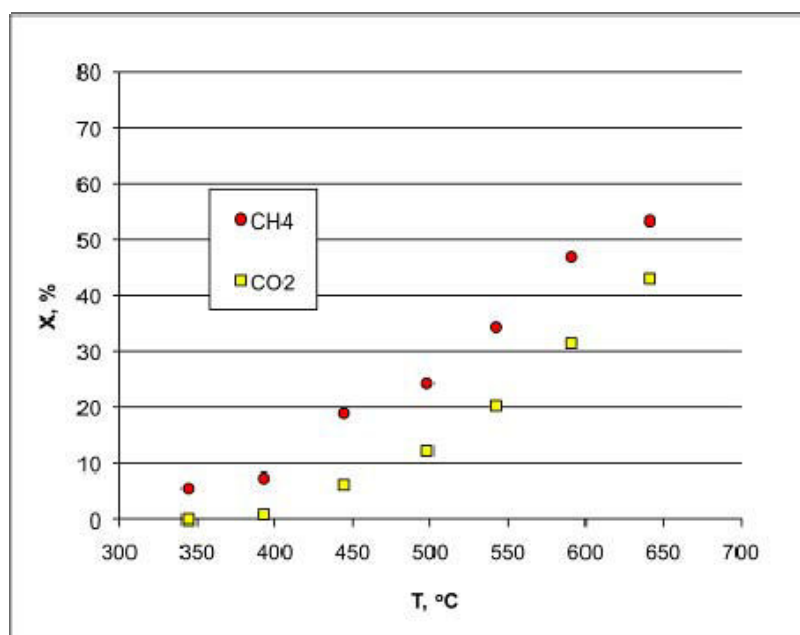
Fig.10. Conversions of methane and carbon dioxide *vs.* temperature on [Pd-Mn]-TiO$_2$/Ni-Al system (W$_{feed}$=40 l/h).

It should be noted that initial temperature of methane conversion on membrane catalytic systems is essentially lower as it could be expected according to the bibliography. In a traditional flow-bed reactor with a bulk layer of the same kind of catalyst the temperature is 750-850°C [35; 36].

In continuous experiment was shown that [La-Ce]-MgO-TiO$_2$/Ni-Al system is capable to work for a long period of time (~ 40 h) without evident decrease in catalytic activity and selectivity (Fig.11).
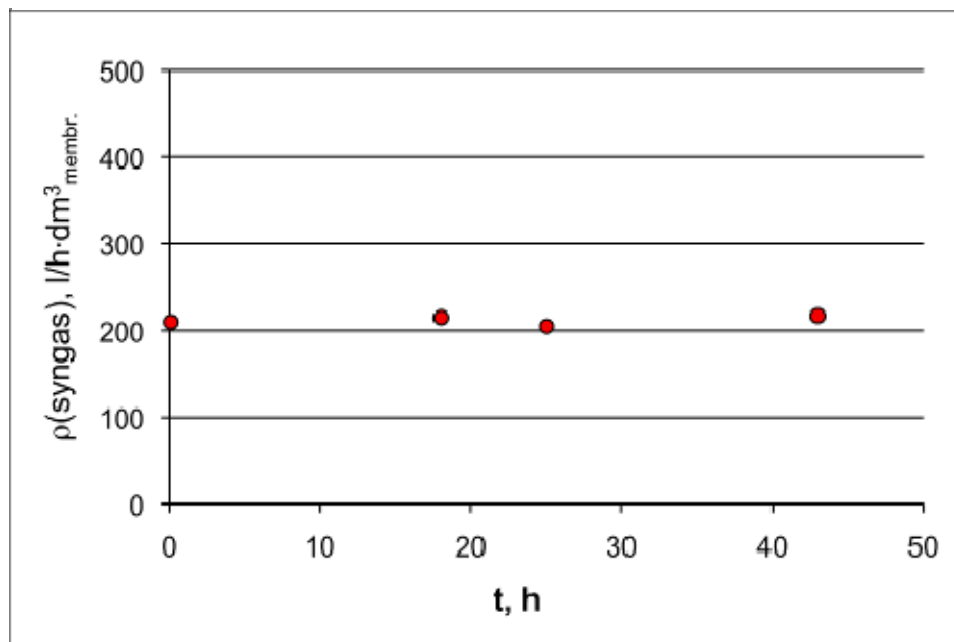
Fig.11. Continuous experiment on [La-Ce]-MgO-TiO$_2$/Ni-Al system. Syngas productivity *vs.* time of experiment (CH$_4$/CO$_2$=1/3, T=650°C, W$_{feed}$=18 l/h, H$_2$/CO=0.3).

3.1.2 Study of DMR dynamics

Dynamics of methane and carbon dioxide conversions on membrane catalytic systems were studied for the purpose of finding direct and indirect reactions in DMR process.

By thermogravimetry was found that essential loss of weight (TG) of virgin Ni-Al membrane during methane pass initiates at temperature ~550°C and it is accompanied by formation of H$_2$, CO, CO$_2$ and H$_2$O (Fig.12).
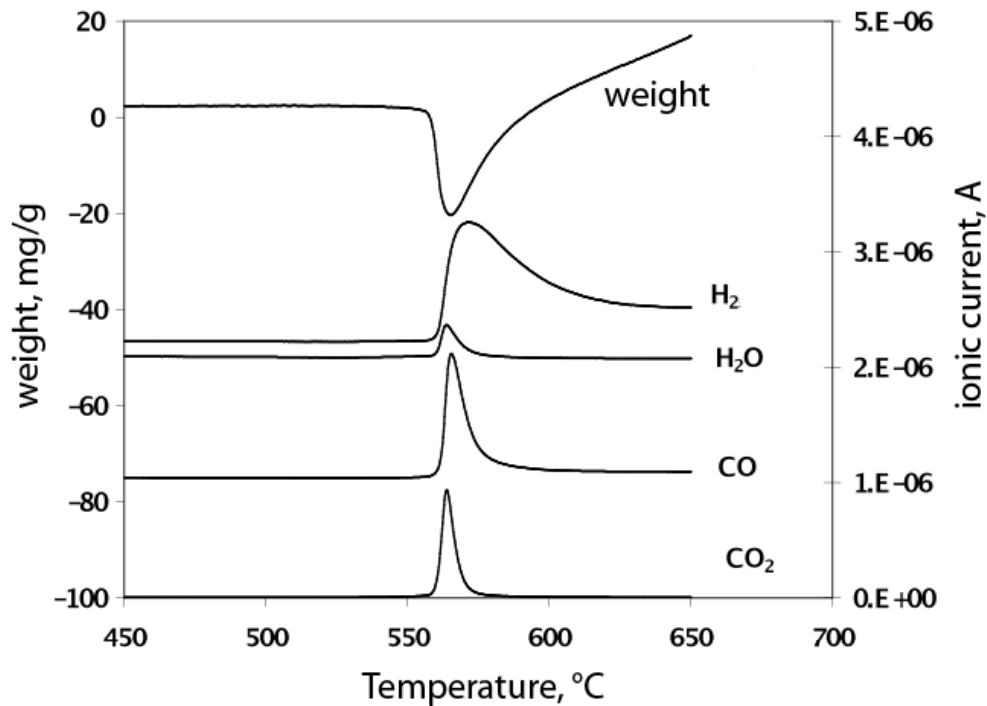
Fig.12. Gravimetric data and products composition of methane conversion at programmed increasing of temperature.

After a time weight of the sample starts to increase up to the temperature maximum (700 °C) with hydrogen formation.

These results make possible to surmise that loss of weight of the membrane during methane pass, probably occurs due to reduction of surface oxides of the sample:

$$CH_4 + 1/2\ O_2 \rightarrow CO + 2H_2$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
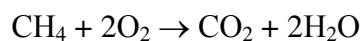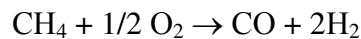
The weight of sample increases because of carbon formation on the surface of the membrane due to reaction of methane dissociation.

$$CH_4 \rightarrow C + 2H_2$$
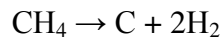
At the following pass of CO_2, weight decrease was noted since 520°C (Fig.13). Treatment of the sample by carbon dioxide was accompanied by formation of carbon monoxide by the reverse reaction of Bell-Boudoir.
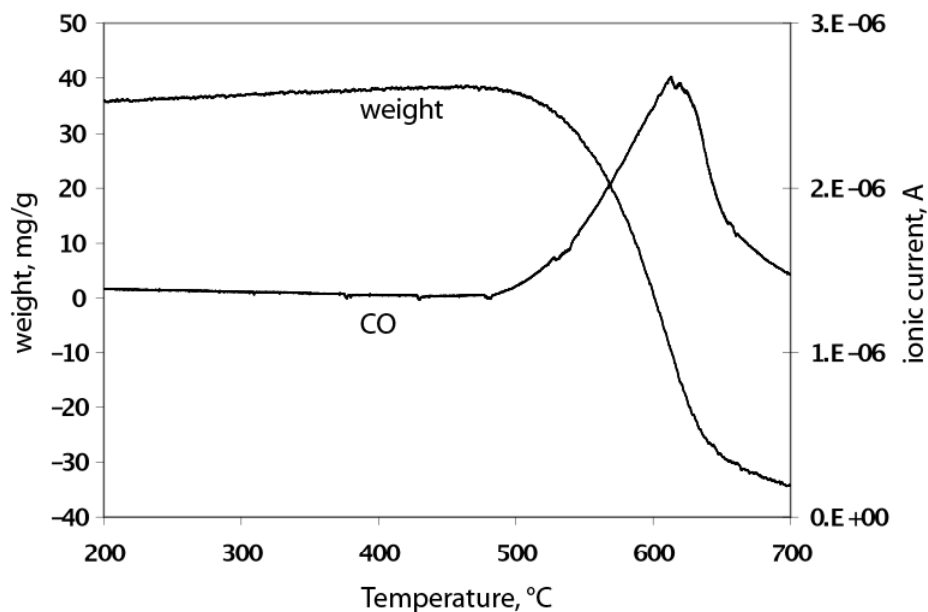
$$C + CO_2 \rightarrow 2CO$$
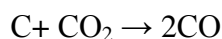
Fig.13. Dynamics of carbon dioxide regeneration process.

Recently it was shown that rate of Bell-Boudoir reaction inside channels of catalytic membranes is about 1.37 mole/dm^3·h, but total rate of methane oxidation is only 0.14 mole/dm^3·h [38].

Reactions order in DMR process on membrane catalytic systems is similar.

In the Fig.14 there are results of experiments on [La-Ce]-MgO/TiO$_2$/Ni-Al catalytic system: curve 1 – the first pass of DMR; curve 2 – carbon dioxide regeneration; curve 3 – the second pass of DMR.
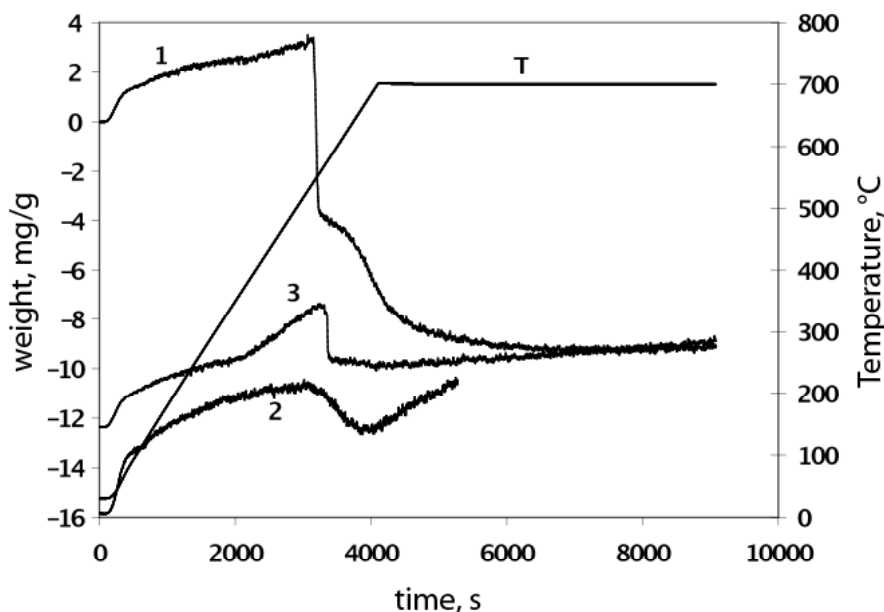
Fig.14. Dynamics of DMR process and carbon dioxide regeneration on [La-Ce]-MgO/TiO$_2$/Ni-Al system.

It was noted that on La-Ce catalytic system process initiates at lower temperature (500°C) in comparison with a virgin membrane. At the maximum temperature of the experiment (700°C) weight of the sample didn't change, it points out that reaction (4) has been finished. But the second pass of carbon dioxide points out reaction with permanent surface carbon (Fig.14, curves 1,2). Incomplete conversion of carbon at the first pass of carbon dioxide points out an external diffusion complications, caused by reactors construction but several treatments of system by carbon dioxide make possible to predetermine total amount of carbon, formatted in DMR process.

At the second pass of DMR (Fig.14, curve 3) system came to the steady-state conditions very quickly. As it is shown on the Fig.15, DMR process on [La-Ce]-MgO/Ni-Al catalytic system is accompanied by formation of H_2, CO and H_2O.
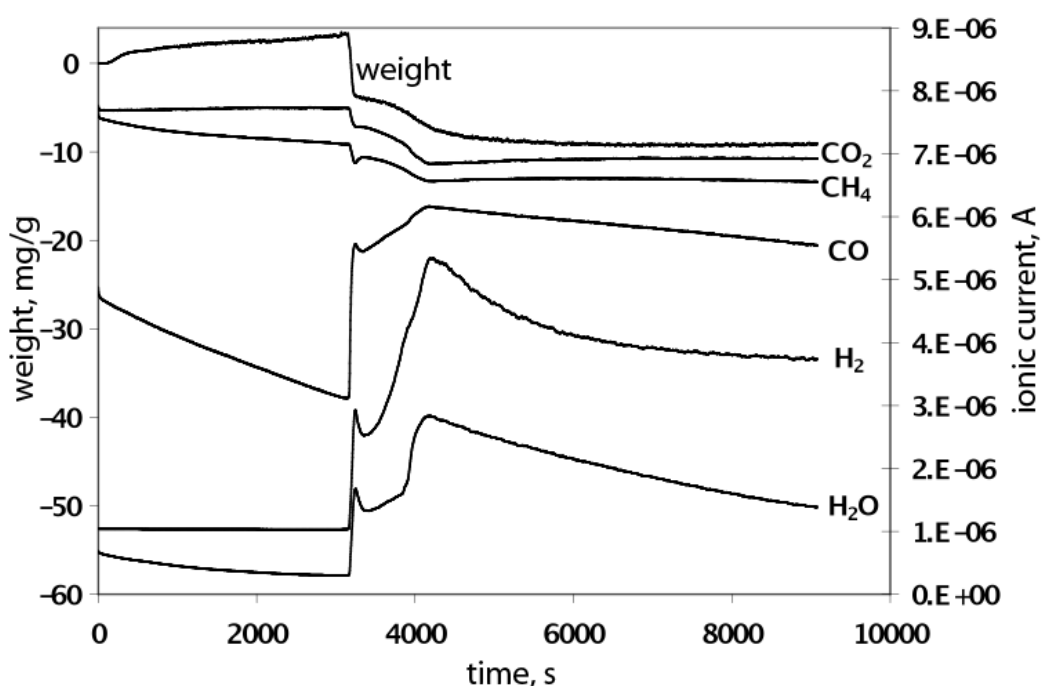

Fig.15. DMR on [La-Ce]-MgO/TiO$_2$/Ni-Al system.

The Fig.15 shows that there is no essential mass change right up the maximum temperature of the experiment (700°C) if the system is in stationary conditions, what is evidence to low share of carbon-producing processes. The next treatment of system by CO_2 proved this hypothesis (Fig.16).
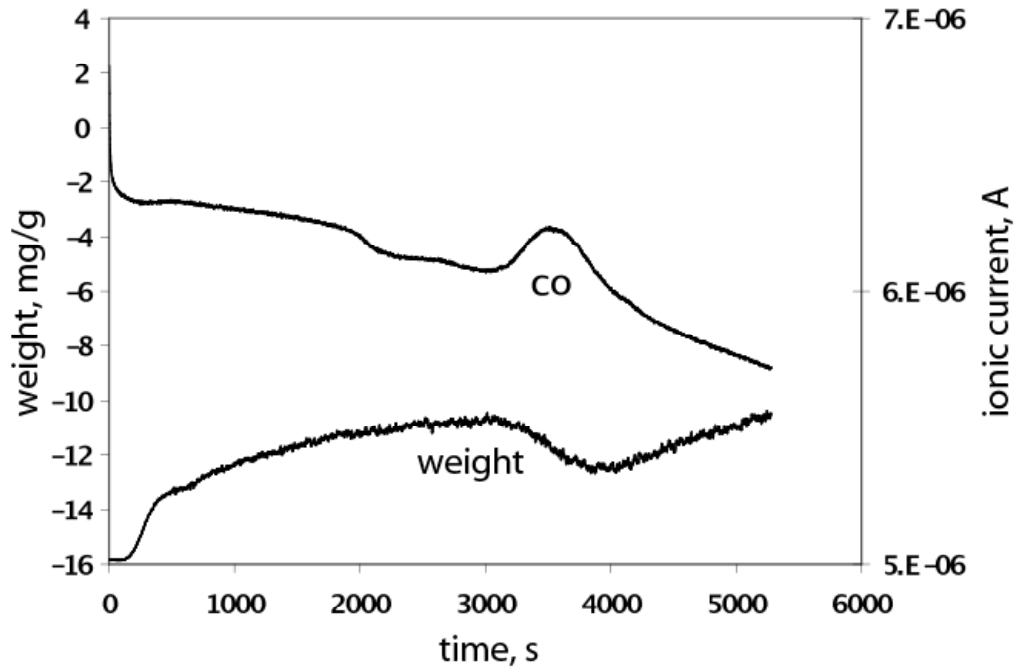
Fig.16. Mass change of [La-Ce]-MgO/TiO$_2$/Ni-Al system and formation of CO by heat-treat in CO$_2$ after DMR process.

In the Fig.17 the same pattern of DMR dynamics studies but for [Pd-Mn]-TiO$_2$/Ni-Al system is represented: curve 1 – the first pass of DMR; curve 2 – carbon dioxide regeneration; curve 3 – the second pass of DMR.
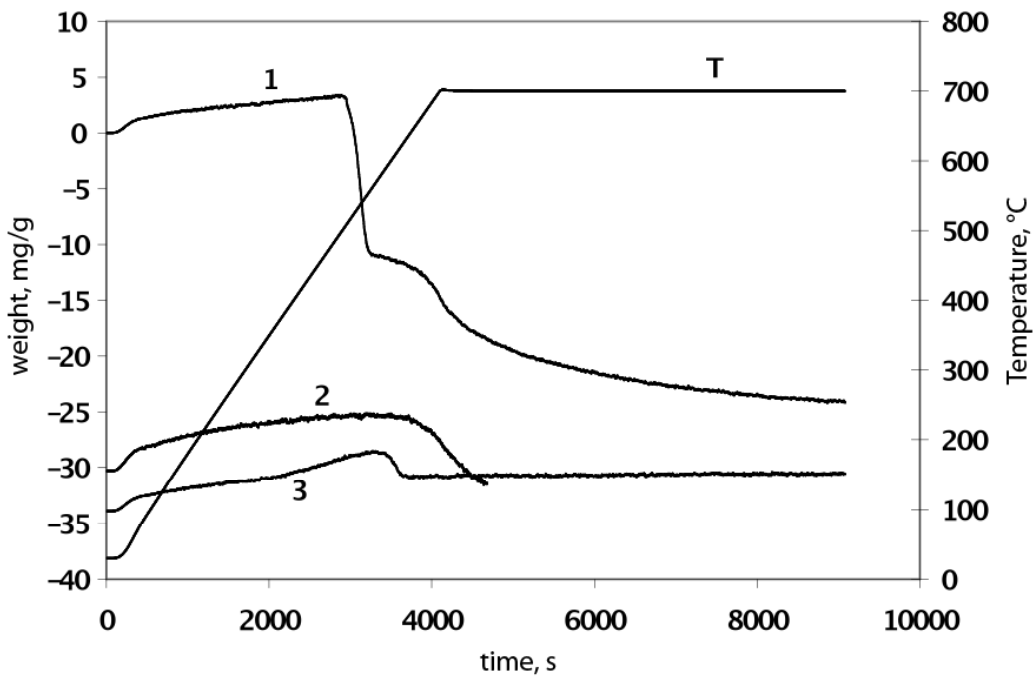

Fig.17. Dynamics of DMR process and carbon dioxide regeneration on [Pd-Mn]-TiO$_2$/Ni-Al system.

Dynamics of DMR process and carbon dioxide regeneration on [Pd-Mn]-TiO$_2$/Ni-Al catalytic system are similar to [La-Ce]-MgO/TiO$_2$/Ni-Al, but share of carbon-producing processes is low most likely due to higher selectivity of the second catalyst.

DMR process on [Pd-Mn]-TiO$_2$/Ni-Al system was also accompanied by formation of hydrogen, carbon monoxide and water by similar reaction scheme (Fig.18).
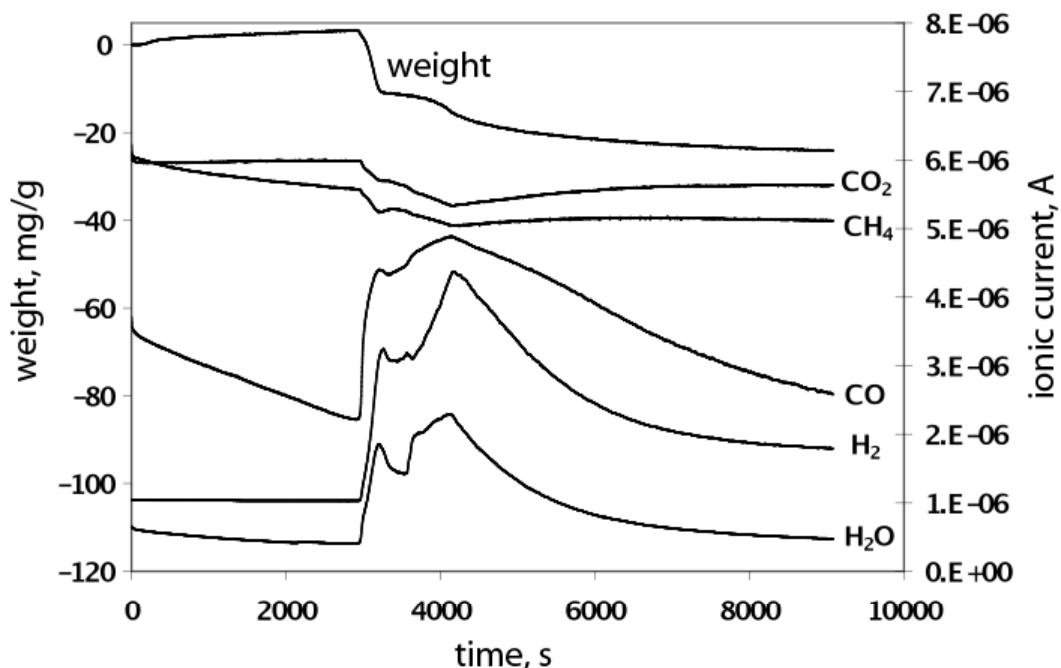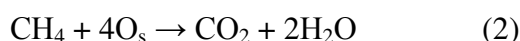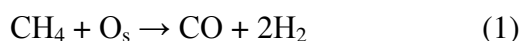

Fig.18. DMR on [Pd-Mn]-TiO$_2$/Ni-Al system.

In the Fig.18 is shown that there is no increase of the sample weight during the DMR process, which is evidence to low share of carbon-producing processes on the catalysts surface. The following pass of CO$_2$ has showed that there are no essential decrease of sample weight and production of carbon monoxide during the process.

Thus, by DMR dynamics study on [La-Ce]-MgO-TiO$_2$/Ni-Al and [Pd-Mn]-TiO$_2$/Ni-Al catalytic systems the following reactions order for the process were proposed:

$$CH_4 + O_s \rightarrow CO + 2H_2 \qquad (1)$$
$$CH_4 + 4O_s \rightarrow CO_2 + 2H_2O \qquad (2)$$
$$CH_4 \rightarrow C + 2H_2 \qquad (3)$$
$$C + CO_2 \rightarrow 2CO \qquad (4)$$

It was shown that DMR initiates methane oxidation by structural oxygen of surface metal oxide phases and CO$_2$ probably reacts with carbon, which obtains by methane dissociation, by reverse Bell-Boudoir reaction (4).

3.1.3 Dry reforming of Fisher-Tropsch synthesis exhaust gases

In dry reforming of Fisher-Tropsch synthesis exhaust gases with composition $C_2 - C_5$ using [La-Ce]-MgO-TiO$_2$/Ni-Al was shown that on the first stage mainly hydrocarbons C_2 — C_5 transform. Increasing of methane concentration after the first stage indicated that they crack. The concentration of carbon dioxide decreased from 17.2 to 10.3%$_{vol.}$. Conversion of CO_2 is 40%. On the 2nd stage concentration of carbon dioxide reduced to 6%$_{vol.}$, conversions are CO_2 – 42%, CH_4 33%. Thus, the total conversion of CO_2 on the two process stages is 65%. The increments of carbon monoxide and hydrogen are 18.3%$_{vol.}$ and 10%$_{vol.}$ correspondingly (Table 3).

Table 3. Dry reforming of Fisher-Tropsch synthesis exhaust gases.

Components	Feed, %$_{vol.}$	Product, %$_{vol.}$ 1st stage	Products, %$_{vol}$ 2nd stage
H_2	40.00	46.63	50
CO	15.69	27.62	34
CH_4	8.06	14.88	10
CO_2	17.23	10.27	6
C_2	2.08	0.56	0
C_2=	0.50	0	0
C_3	0.79	0.05	0
C_3=	1.14	0.01	0
iC_4	0.20	0	0
C_4	0.38	0.01	0
C_4=	0.10	0	0
iC_4=	0,03	0	0
tC_4=	0.09	0	0
iC_5	0.21	0	0
C_5	0.03	0	0
Non-identified gas products	13,5	0	0
SUM:	**100**	**100**	**100**

3.1.4 Dry reforming of light hydrocarbons

It was shown that in dry reforming with steam of light hydrocarbons using applied Pd, Pd-Co, Pd-Mn and Au-Ni catalysts drastic destructions of C_1-C_4 take place (Table 4). These results were used for development of a syngas generator for energy production in integral scheme with firm oxide fuel cell using MCS.

Table 4. Dry reforming with steam of light hydrocarbons.

components	$C_{feed.}$, %$_{vol.}$	T=800°C, W_{feed}=25000 h^{-1}							
		Pd		Pd-Co		Mn		Au-Ni	
		C, %$_{vol.}$	X, %$_{vol.}$	C, %$_{vol.}$	X, %$_{vol.}$	C, %$_{vol.}$	X, %$_{vol.}$	C, %$_{vol.}$	X, %$_{vol.}$
CH_4	2,12	0.29	89.6	0.76	70.5	0.65	76.00	0.54	74.52
C_2H_4	4,16	0	100	0	100	0	100	0.10	97.55
C_3H_6	0,72	0	100	0	100	0	100	-	99.81
C_4H_{10}	0,56	0	100	0	100	0	100	-	99.97
H_2	0	38.85	-	35.85	-	36.23	-	41.59	-
CO	9,41 (6,63 for Au-Ni)	8.19	4.99	6.37	20.42	6.46	21.26	30	-
CO_2*	2,12	14.31	-16.93	15.71	-38.24	16.02	-37.55	-	-

3.2 Study of gas transport and structures of membrane catalytic systems

3.2.1 Gas permeability

Study of gas permeability through membrane catalytic systems by volumetric method at the room temperature with use of air as model gas showed that during DMR there is no essential changes of gas transport parameters for virgin Ni-Al membrane, it shows that carbon formation processes inside channels are slight (Fig.19).
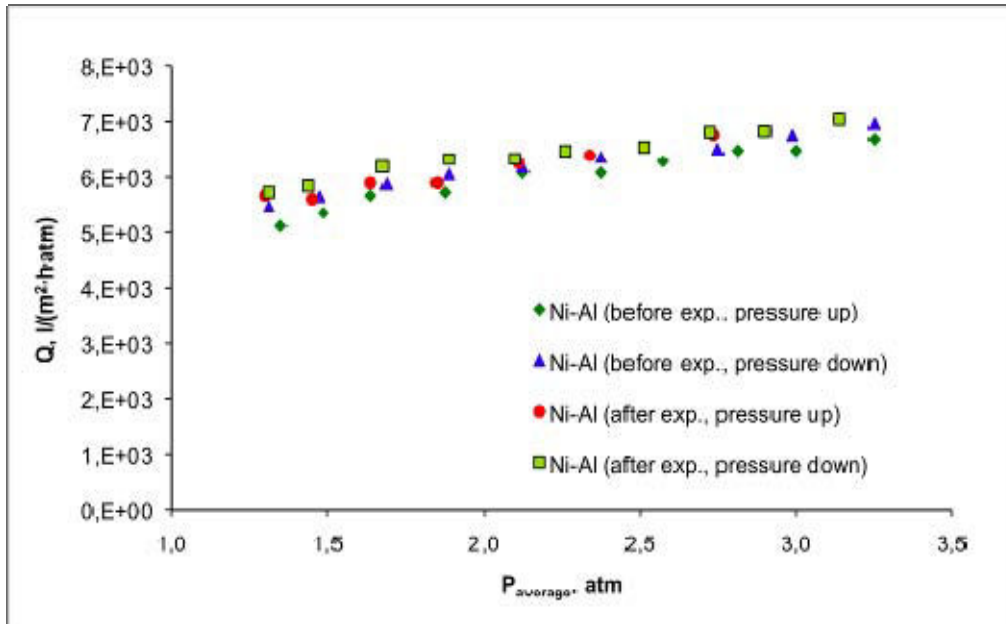
Fig.19. Permeability *vs.* average pressure for Ni-Al membrane before and after DMR ($t_{exp.DMR}$=190 min).

3.2.2 Scanning electron microscopy with energy-dispersive x-ray spectroscopy

By use of SEM+EDX structure of ceramic membranes was studied. Maps of element distribution on the surface of membrane material were arranged.

1) Virgin Ni-Al membrane;
2) [La-Ce]-MgO-TiO$_2$/Ni-Al MCS;
3) [Pd-Mn]-TiO$_2$/Ni-Al MCS.

Sample 1: Ni-Al

In the Fig.20, 21 is shown that membrane structure is porous and granular, it consists of big and small particles.

30
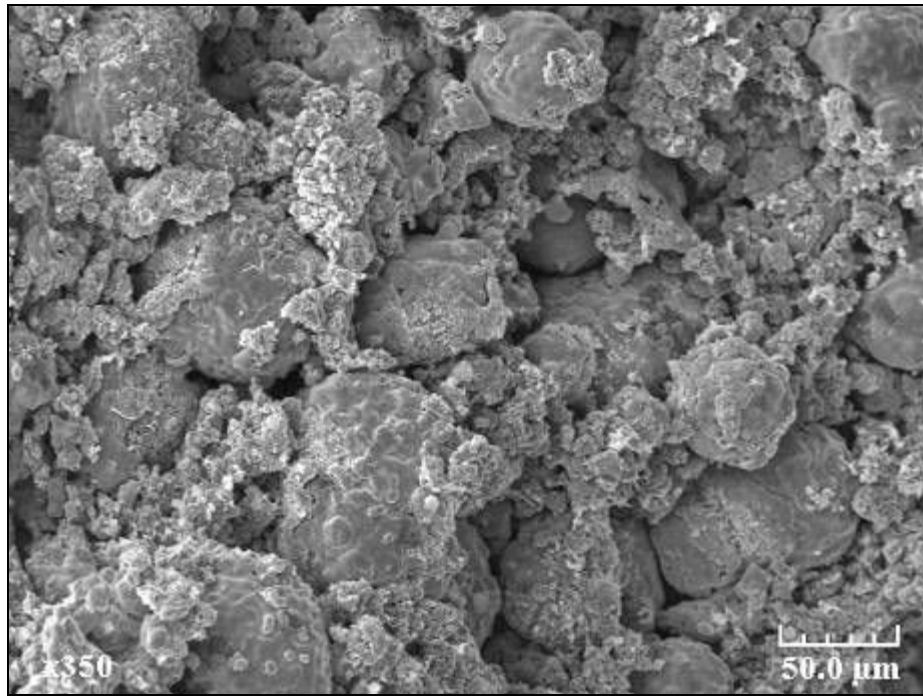
Fig.20. Ni-Al, scale 50 µm.
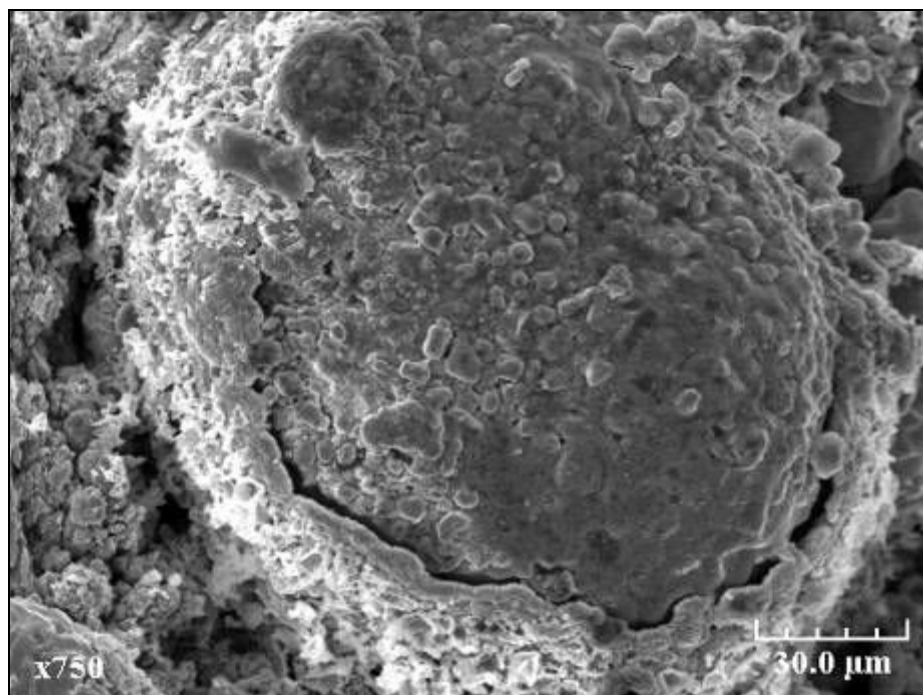
Fig.21. Ni-Al, scale 30 µm. Prescanning surface.

Element composition and distribution of elements on membrane surface has been done by electron topography (EDX). In the Fig.22, 23 are shown that Al particles are in many times smaller than particles of Ni, but at the same time they are not completely separate from each other and represent an alloy.
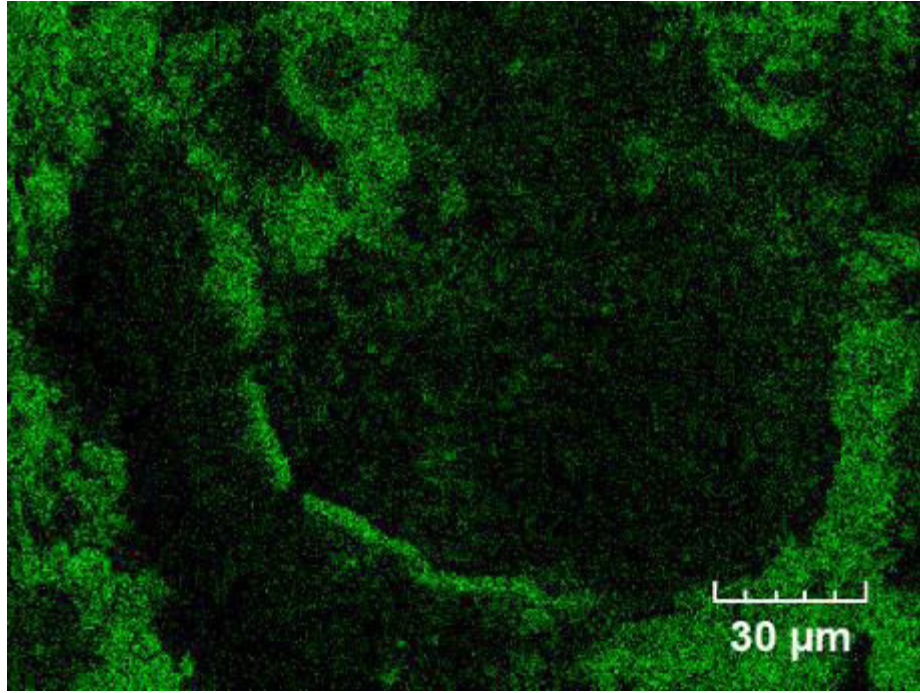
31

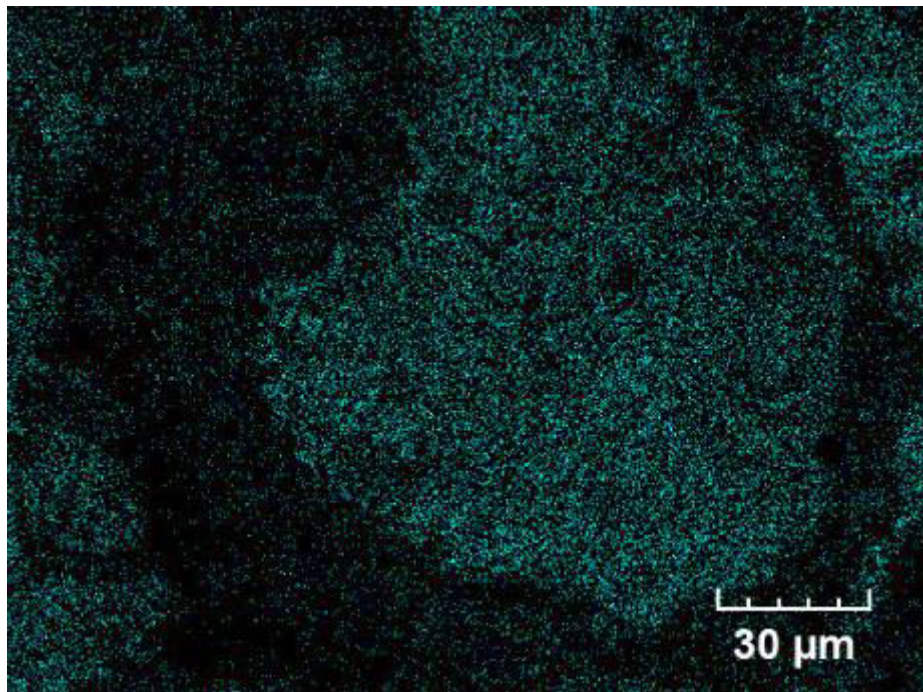Fig.22. Ni-Al, scale 30 µm. Distribution of Al on the scanning sample surface.

Fig.23. Ni-Al, scale 30 µm. Distribution of Ni on the scanning sample surface.

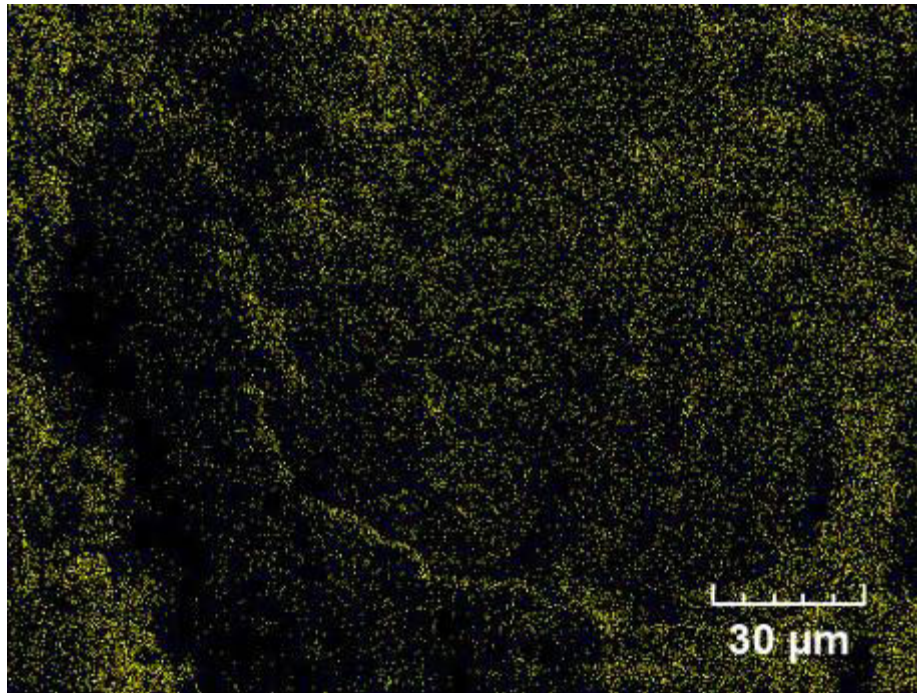In the Fig.24 distribution of oxygen is shown. Apparently, nickel is oxydized more than Al.

Fig.24. Ni-Al, scale 30 µm. Distribution of O on the scanning sample surface.

Sample 2: [La-Ce]-MgO-TiO$_2$/Ni-Al

In the Fig.25-27 are shown that there is no evident differences in membrane structure between modified membrane and the virgin one.
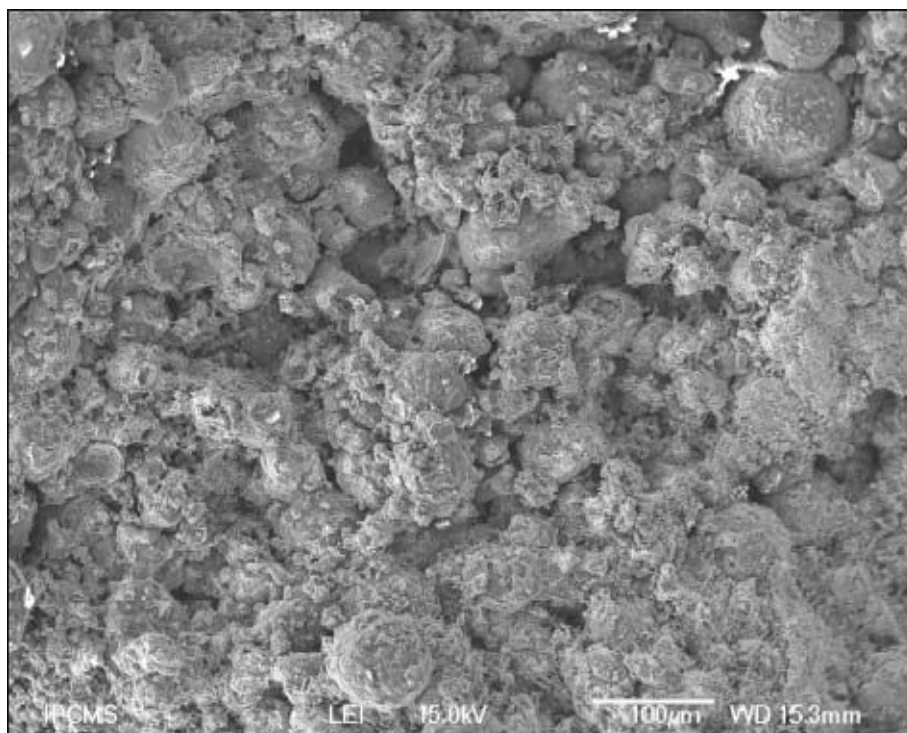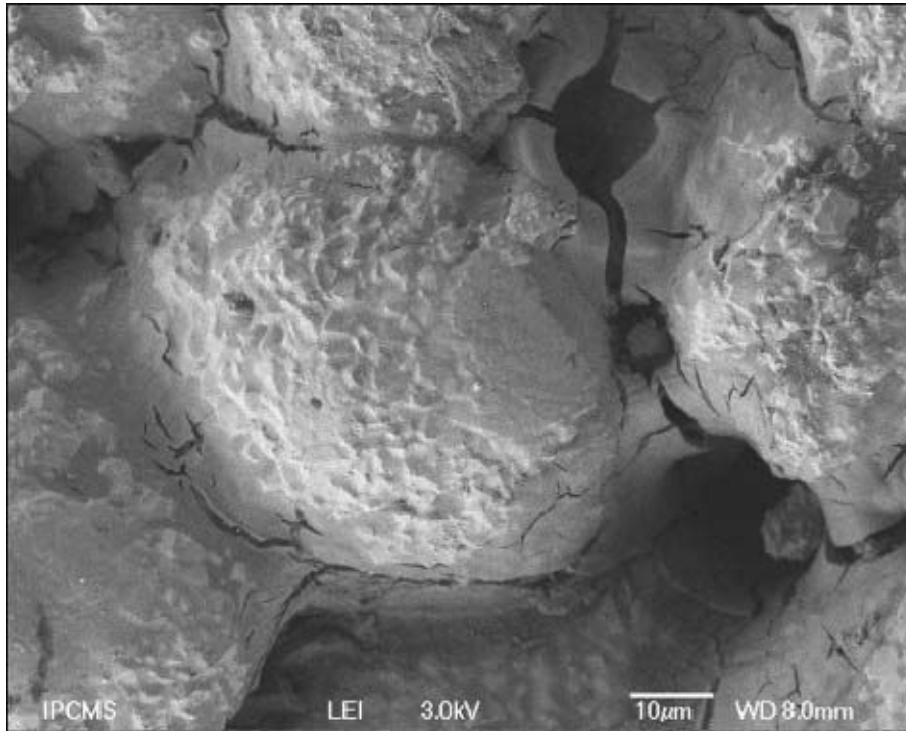

Fig.25. [La-Ce]-MgO-TiO$_2$/Ni-Al, scale 100 µm.
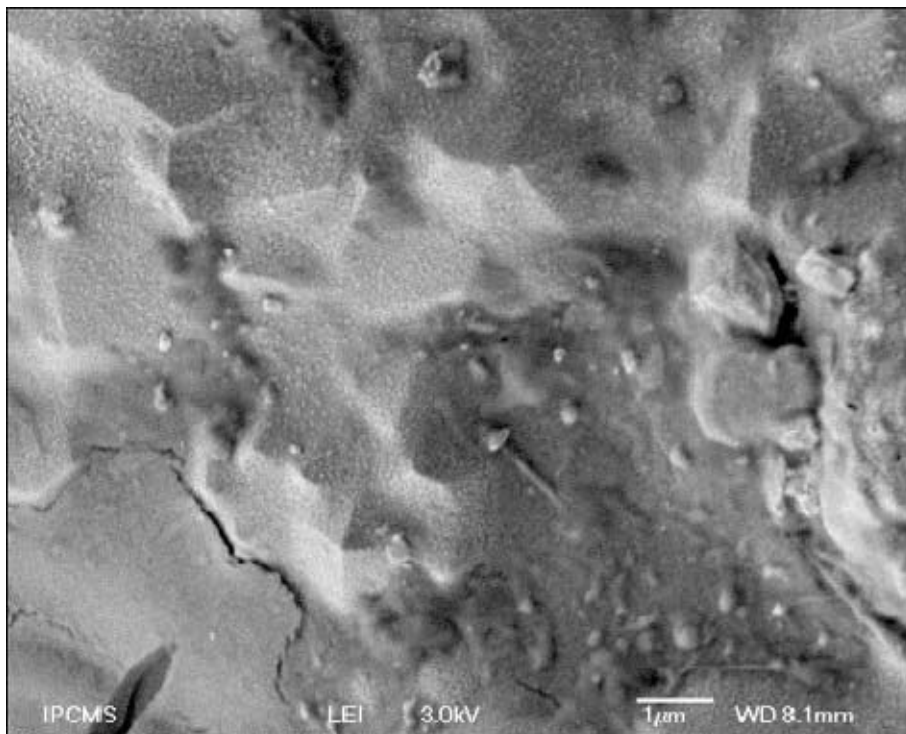
Fig.26. [La-Ce]-MgO-TiO$_2$/Ni-Al, scale 10 µm.
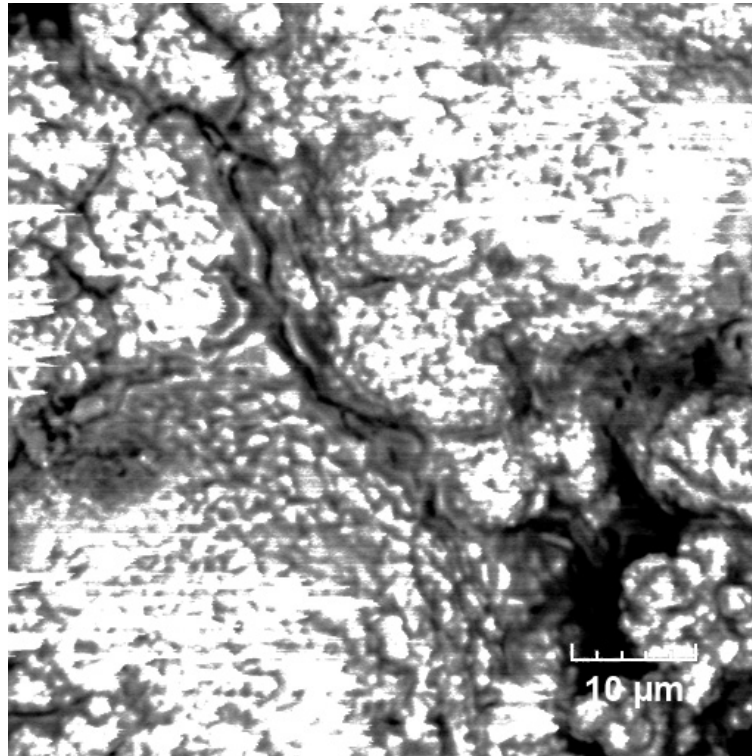

Fig.27. [La-Ce]-MgO-TiO$_2$/Ni-Al, scale 1 µm.

Fig.28. [La-Ce]-MgO-TiO$_2$/Ni-Al, scale 10 µm. Prescanning surface.

In the Fig.29,30 are shown that catalytic active components, La and Ce, are distributed uniformly on the mebrane surface (Fig.28).
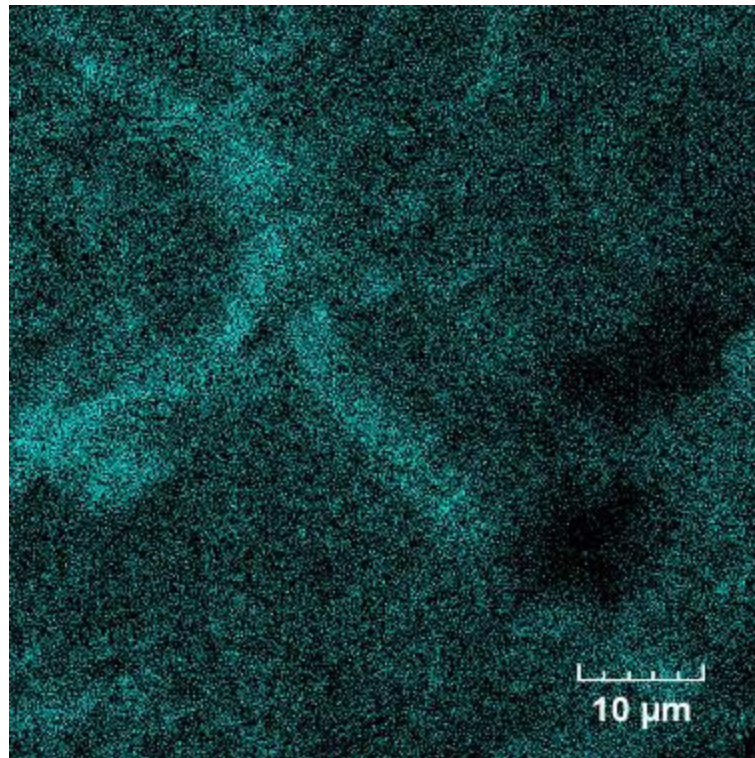

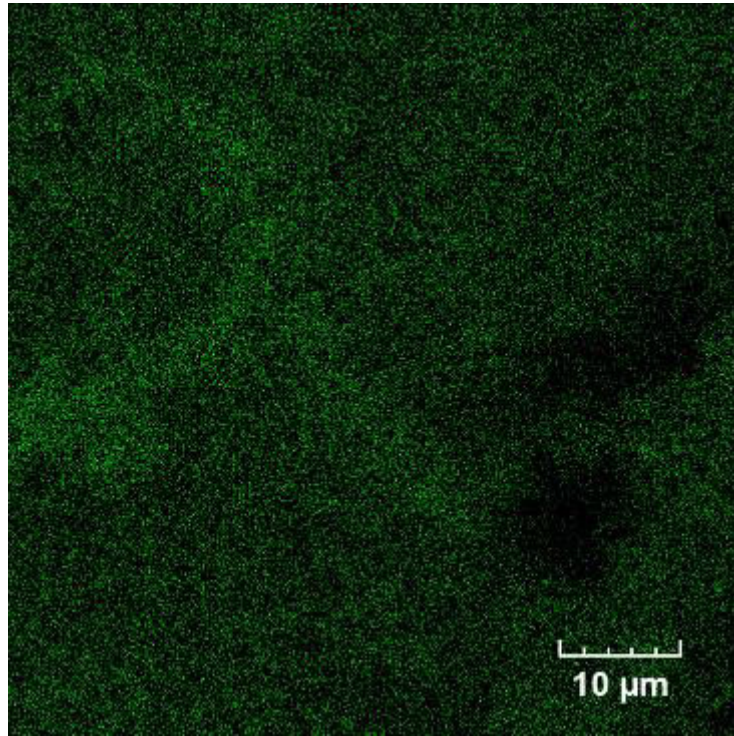Fig.29. [La-Ce]-MgO-TiO$_2$/Ni-Al, scale 10 µm. Distribution of La on the scanning sample surface.

Fig.30. [La-Ce]-MgO-TiO$_2$/Ni-Al, scale 10 µm. Distribution of Ce on the scanning sample surface.

In the Fig.31 distribution of Mg catalytic base is represented. It is obvious that Mg fixes ruptures in membrane surface.
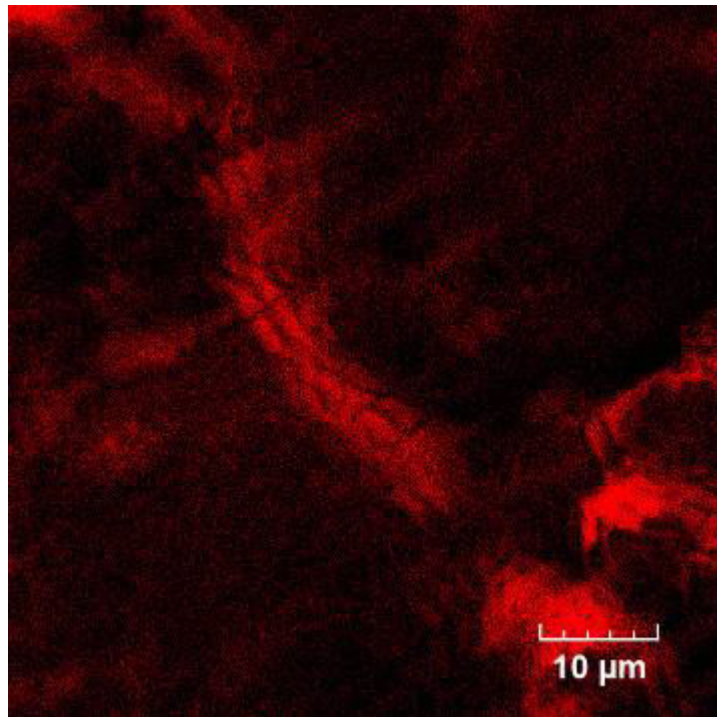
Fig.31. [La-Ce]-MgO-TiO$_2$/Ni-Al, scale 10 µm. Distribution of Mg on the scanning sample surface.

Next figures ([Fig.32](#), [33](#), [34](#)) show that oxygen is well distributed on the membrane surface, it means that all surface metals are in oxide phases.
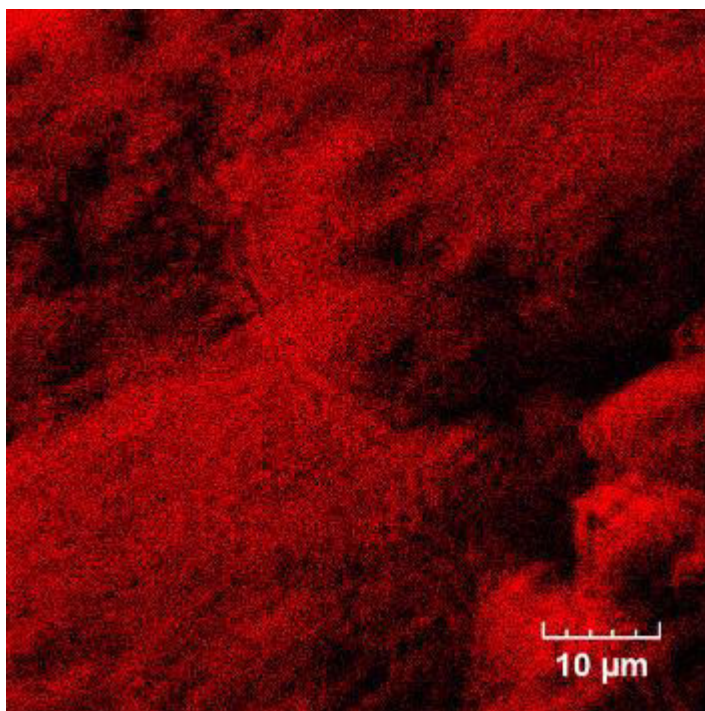
Fig.32. [La-Ce]-MgO-TiO$_2$/Ni-Al, scale 10 µm. Distribution of O on the scanning sample surface.
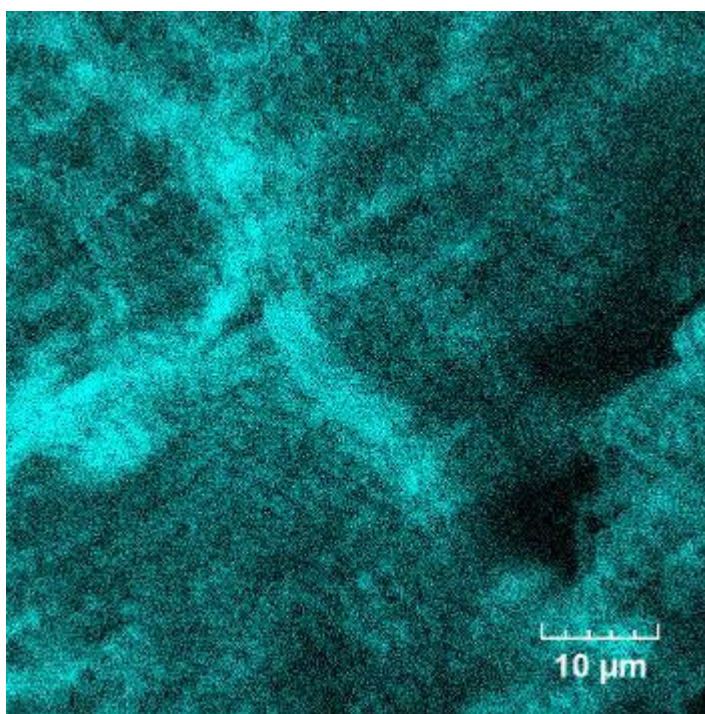
Fig.33. [La-Ce]-MgO-TiO$_2$/Ni-Al, scale 10 µm. Distribution of Ti on the scanning sample surface.

Fig.34. [La-Ce]-MgO-TiO$_2$/Ni-Al, scale 10 µm. Distribution of Ni on the scanning sample surface.

Fig.35 shows that aluminium particles are small.
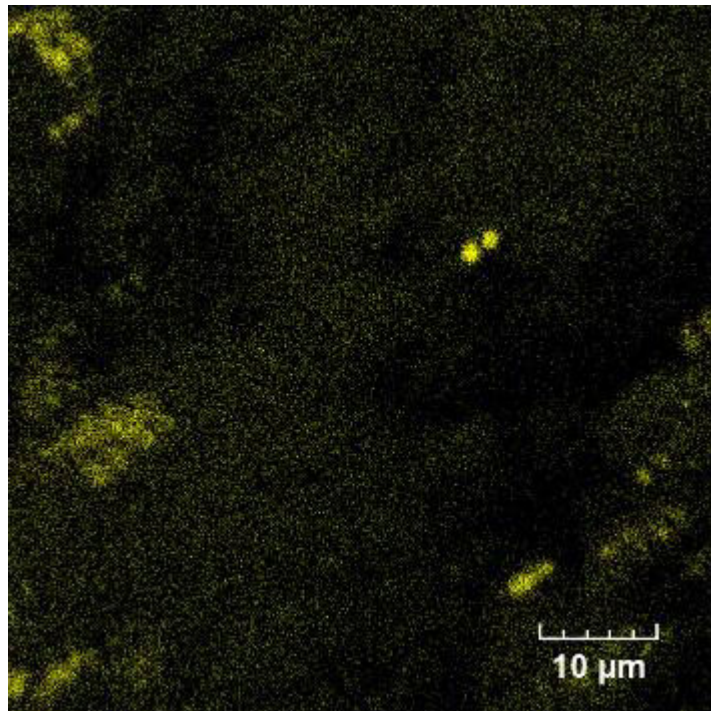
Fig.35. [La-Ce]-MgO-TiO$_2$/Ni-Al, scale 10 µm. Distribution of Al on the scanning sample surface.

Sample 3: [Pd-Mn]-TiO$_2$/Ni-Al
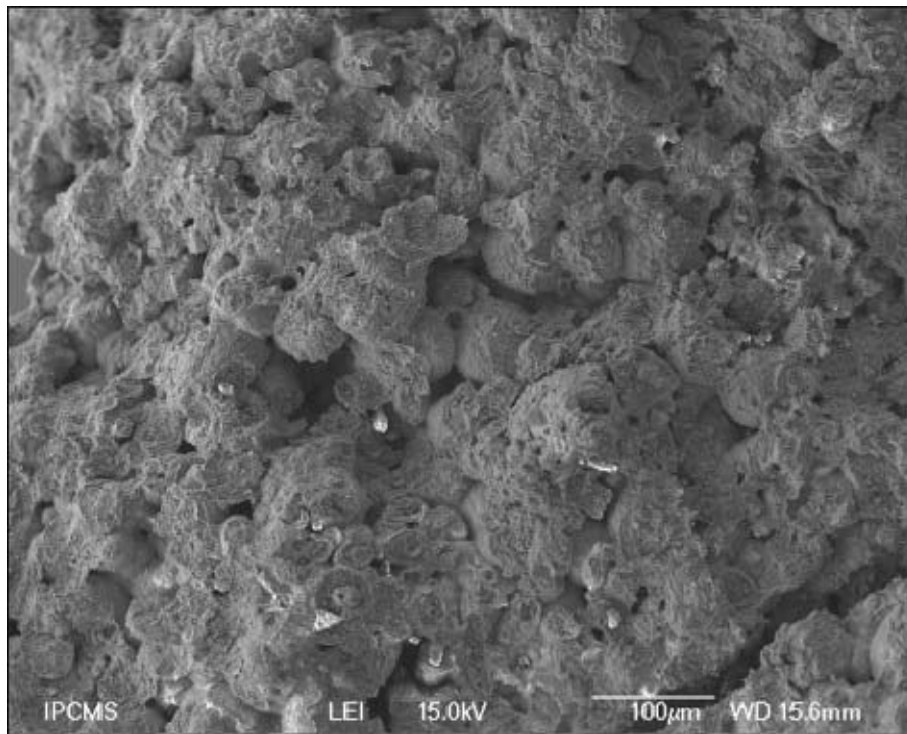
Fig.36. [Pd-Mn]-TiO$_2$/Ni-Al, scale 100 µm.
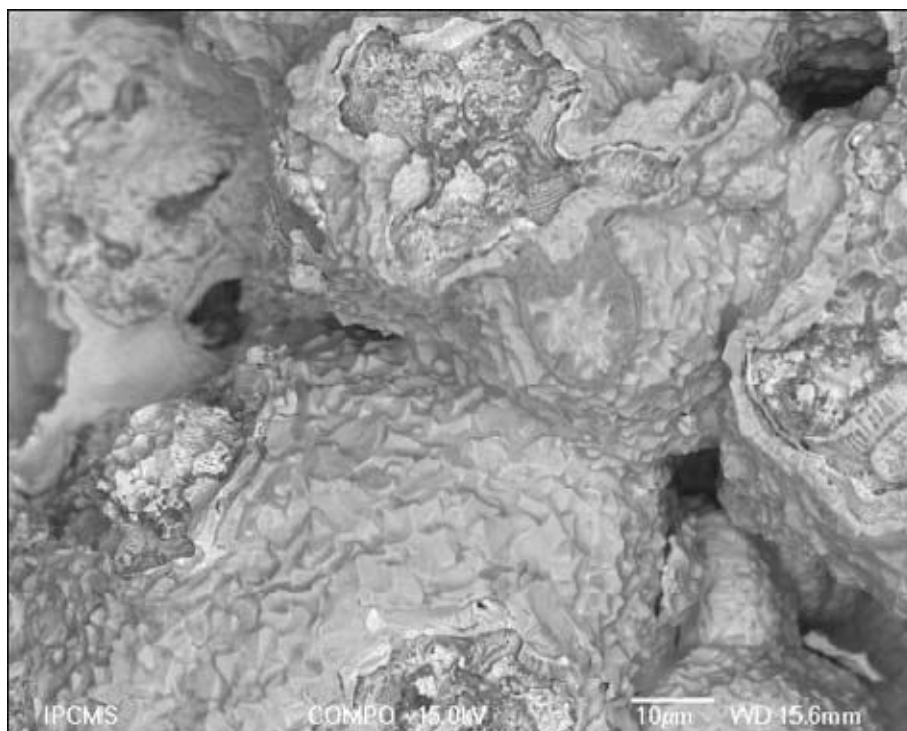
Fig.37. [Pd-Mn]-TiO$_2$/Ni-Al, scale 10 µm.
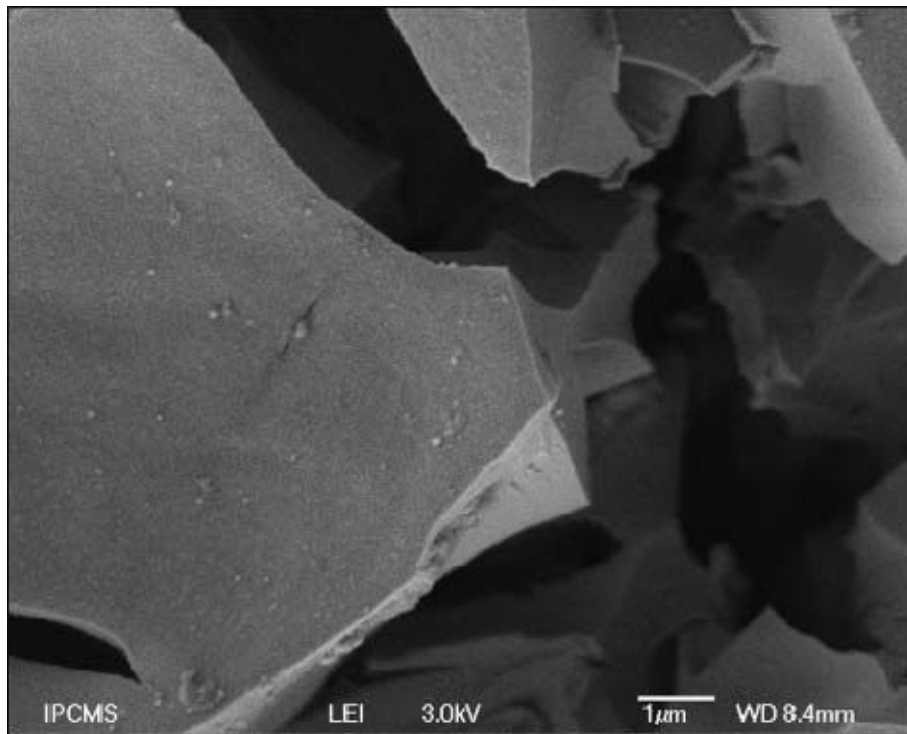
Fig.38. [Pd-Mn]-TiO$_2$/Ni-Al, scale 1 µm.
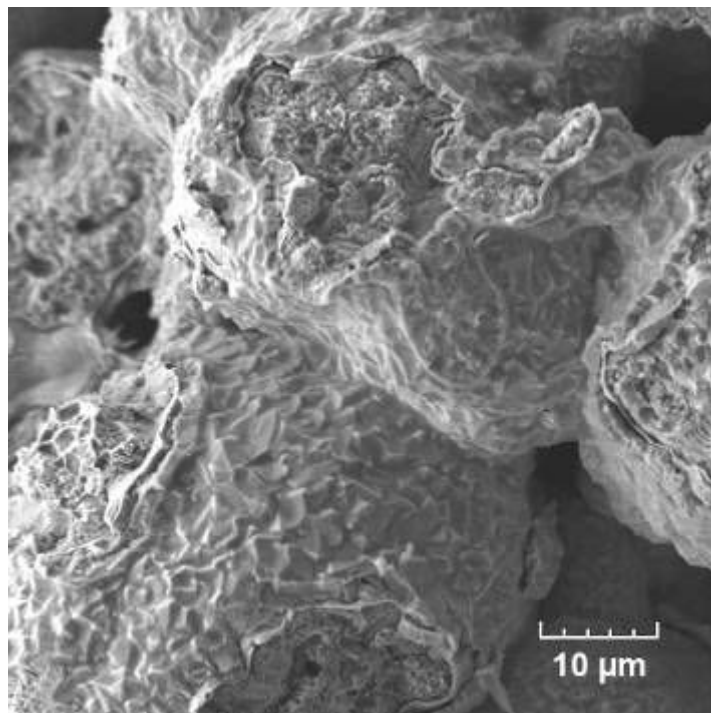
Fig.39. [Pd-Mn]-TiO$_2$/Ni-Al, scale 10 µm. Prescanning surface.

In the Fig.40, 41 are shown that Pd and Mn are distributed uniformlia ans that they cover the same areas of membrane surface.
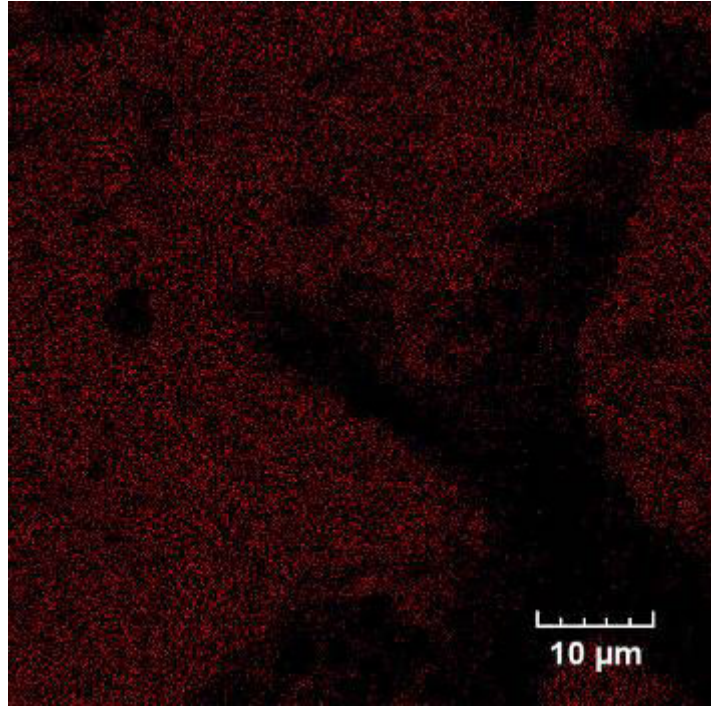
Fig.40. [Pd-Mn]-TiO$_2$/Ni-Al, scale 10 µm. Distribution of Pd on the scanning sample surface.
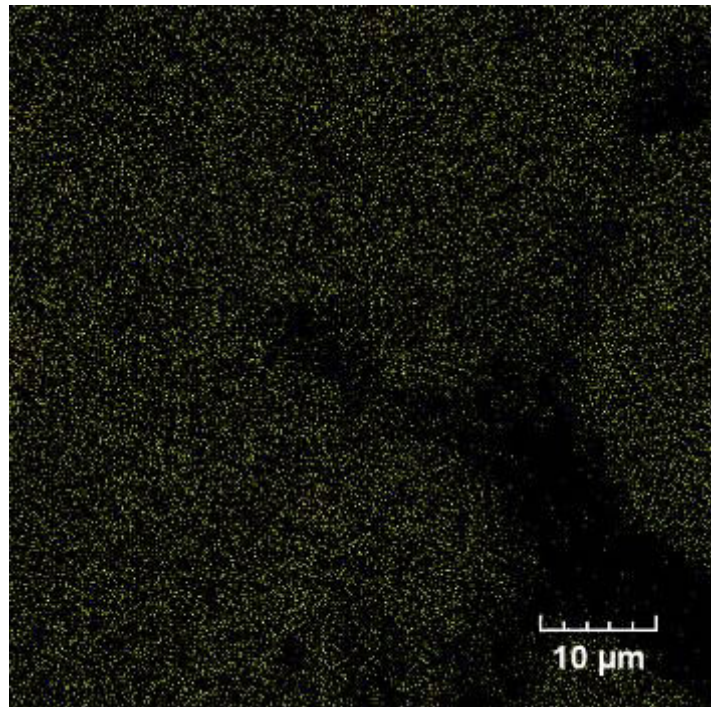
Fig.41. [Pd-Mn]-TiO$_2$/Ni-Al, scale 10 µm. Distribution of Mn on the scanning sample surface.

In the Fig.42 is shown that Ti base mainly covers big particles.

41
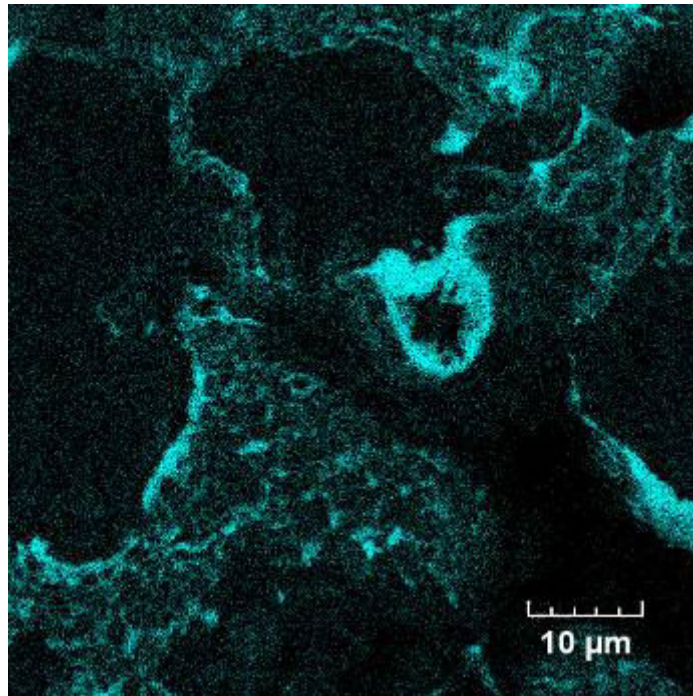
Fig.42. [Pd-Mn]-TiO$_2$/Ni-Al, scale 10 µm. Distribution of Ti on the scanning sample surface.

The Fig.43 reaffirms that syrface of MCS is oxydized.
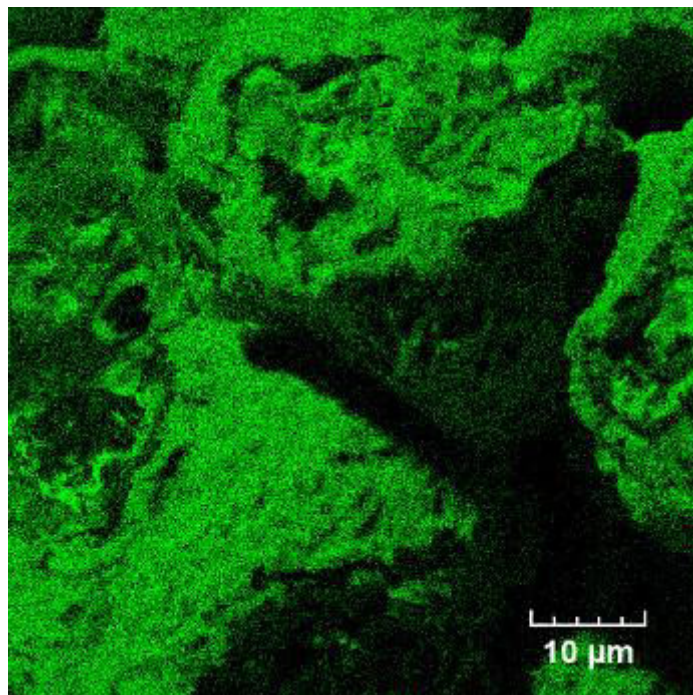
Fig.43. [Pd-Mn]-TiO$_2$/Ni-Al, scale 10 µm. Distribution of O on the scanning sample surface.

Fig.44 and 45 prove that big particles are made of nickel and small ones of aluminum.
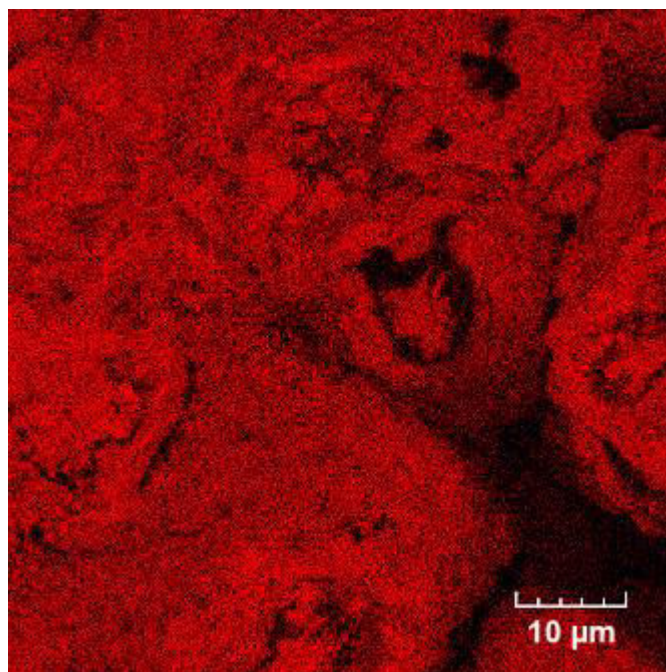
Fig.44. [Pd-Mn]-TiO$_2$/Ni-Al, scale 10 µm. Distribution of Ni on the scanning sample surface.
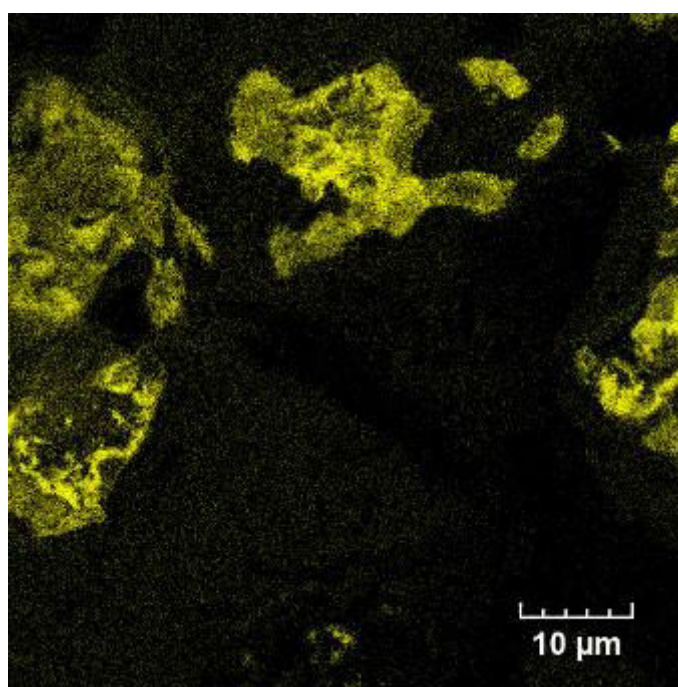
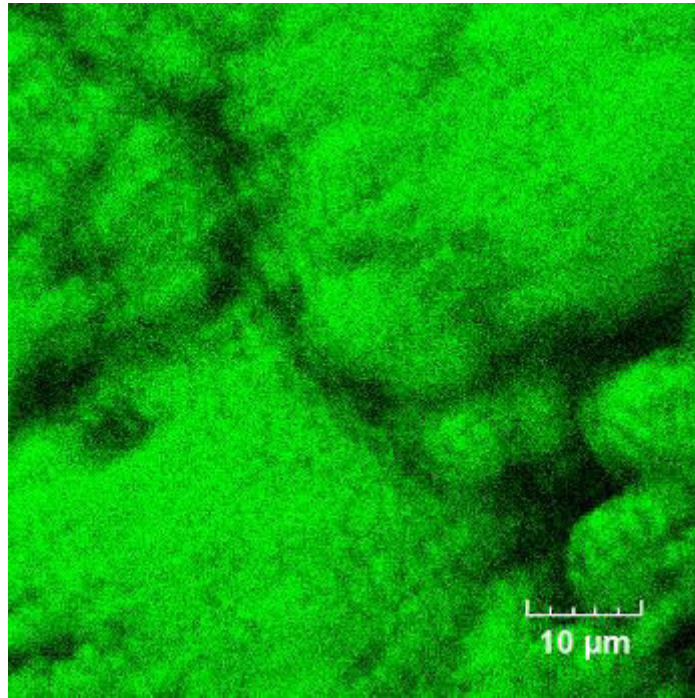Fig.45. [Pd-Mn]-TiO$_2$/Ni-Al, scale 10 µm. Distribution of Al on the scanning sample surface.

It was found that metal oxide catalysts are applied uniformly, structural oxygen, which initiates DMR, was identified.

As a result of experiment it was found that microstructure of MCS doesn't undergo apparent changes after catalyst application. Surface has granular morphology; particles have different size and composition.

In the figures above is shown that big granules are mainly composed of nickel and small from aluminum. Oxygen on the surface is distributed uniformly, that indirectly points that membrane material is oxidized. According to method of membrane production, oxide phases are the binding components, providing mechanical durability of the material. Studying of DMR dynamics has shown that process is initiated by oxidation of methane. On the basis of SEM-EDX data it is possible to make an assumption that surface oxygen (O_s) participates in the reaction.

It was also found La-Ce and Pd-Mn catalysts are distributed on the membrane surface uniformly, that proves efficiency of sol-gel method for metal surface modification by active components.

3.2.3 Transmission Electron Microscopy

By TEM local structure of following MCS was studied:
1) [La-Ce]-MgO-TiO_2/Ni-Al;
2) [Pd-Co]-TiO_2/Ni-Al.

Sample 1: [La-Ce]-MgO-TiO$_2$/Ni-Al
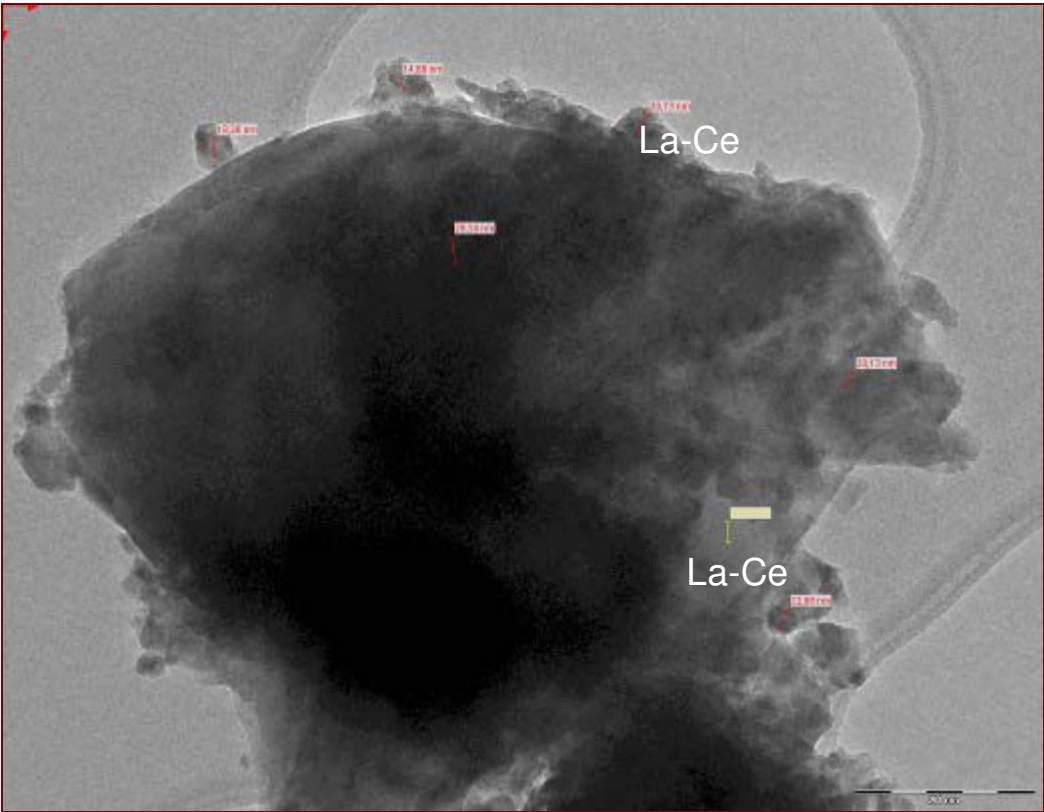
Fig.46. [La-Ce]-MgO-TiO$_2$/Ni-Al, scale 200 nm.
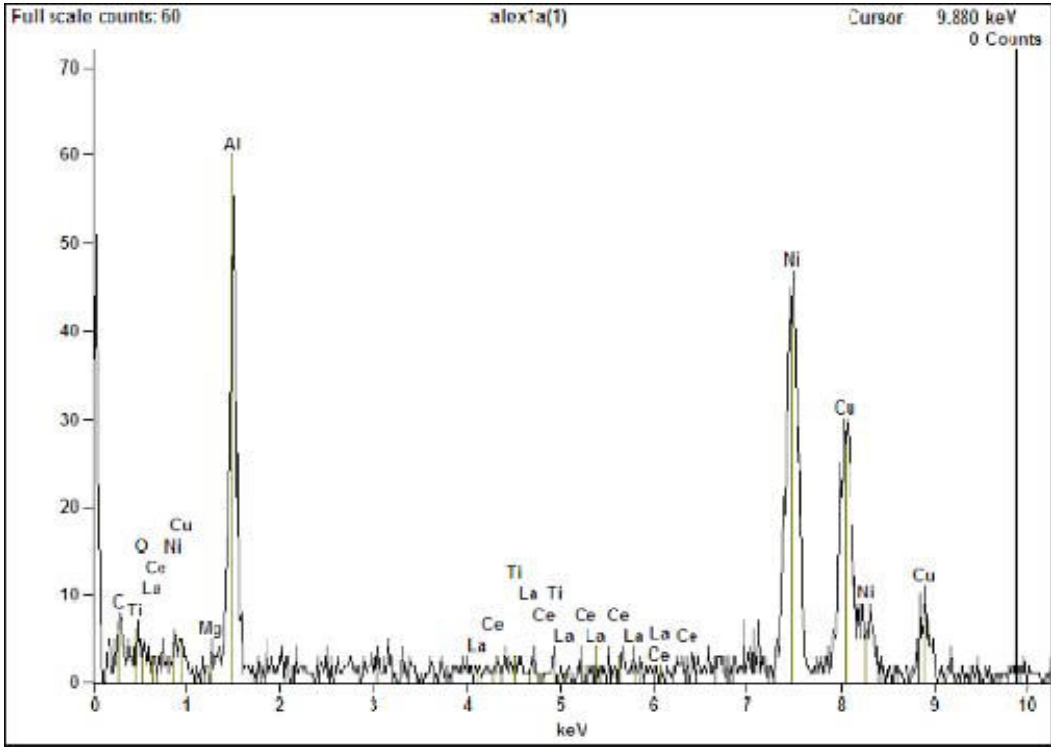
Fig.47. [La-Ce]-MgO-TiO$_2$/Ni-Al.

Table.5. Local composition of [La-Ce]-MgO-TiO$_2$/Ni-Al.

Element Line	Weight %	Weight % Error	Atom %	Atom % Error	Formula	Compnd %
Mg K	0.28	+/- 0.28	0.47	+/- 0.47	Mg	0.28
Al K	35.32	+/- 1.77	54.07	+/- 2.71	Al	35.32
Ti K	0.91	+/- 0.45	0.78	+/- 0.39	Ti	0.91
Ni K	63.50	+/- 2.46	44.68	+/- 1.73	Ni	63.50
Total	100.00		100.00			100.00

It was shown by local analysis that average size of La-Ce cluster is about 20 nm.

Sample 2: [Pd-Co]-TiO$_2$/Ni-Al
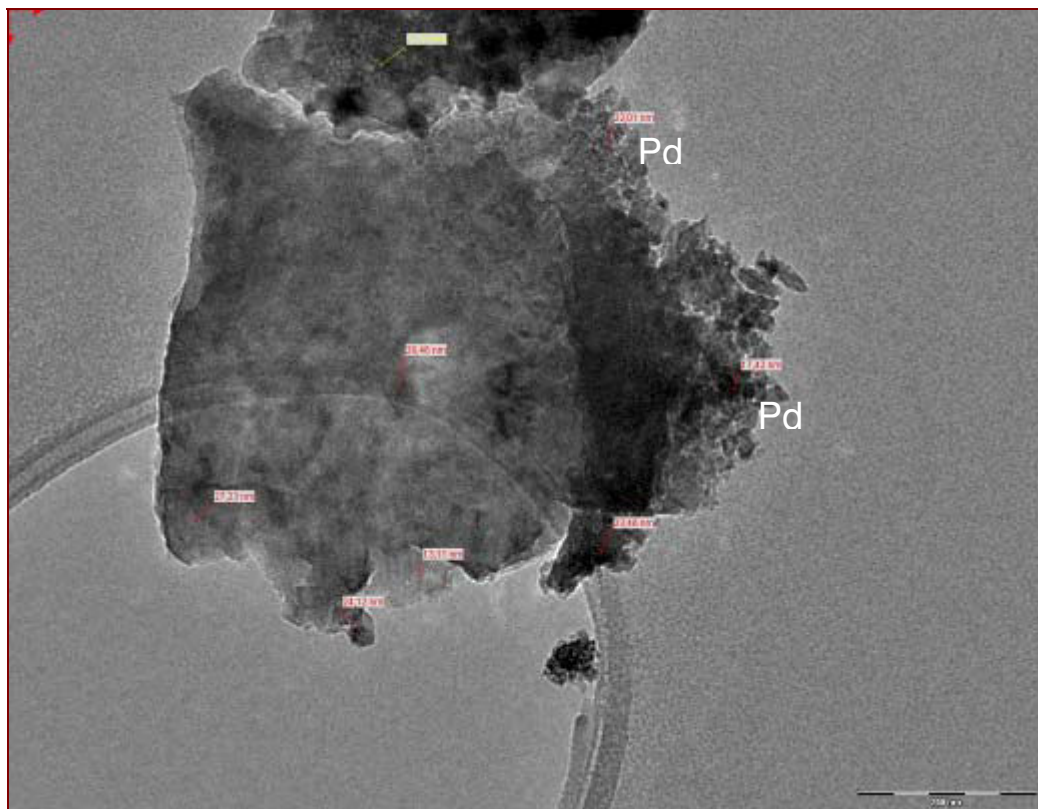
Fig.48. [Pd-Co]-TiO$_2$/Ni-Al, scale 200 nm.
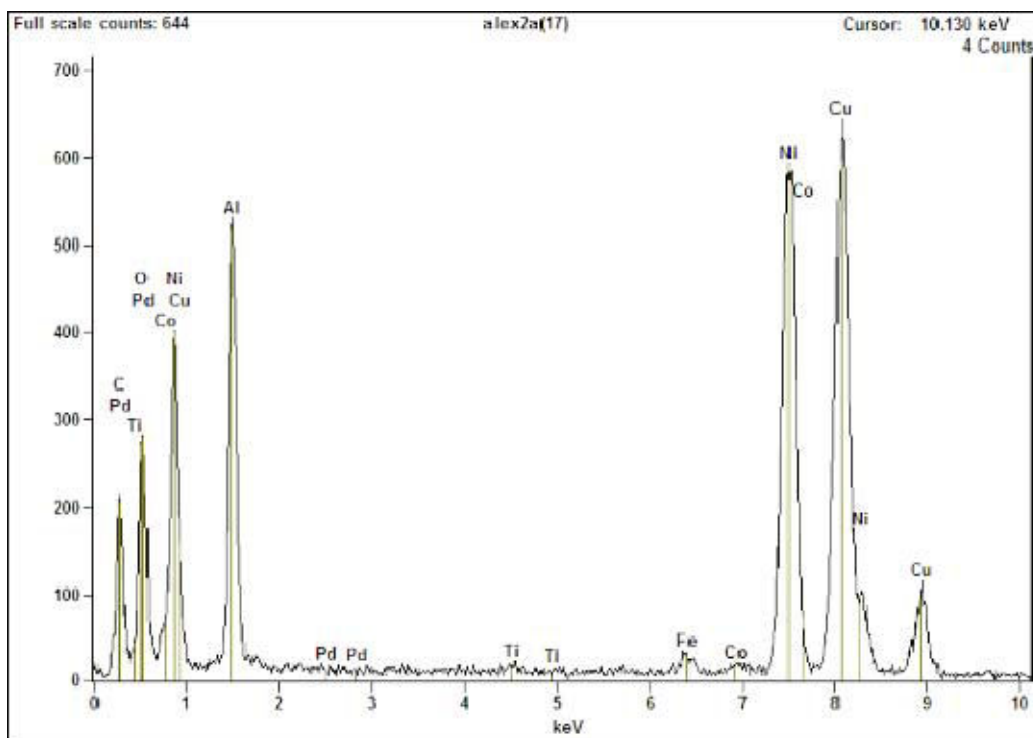
Fig.49. [Pd-Co]-TiO$_2$/Ni-Al.

Table.6. Local composition of [Pd-Co]-TiO$_2$/Ni-Al.

Element Line	Weight %	Weight % Error	Atom %	Atom % Error	Formula	Compnd %
Al K	30.47	+/- 0.45	48.82	+/- 0.73	Al	30.47
Co K	1.04	+/- 0.13	0.77	+/- 0.10	Co	1.04
Ni K	68.48	+/- 0.69	50.42	+/- 0.51	Ni	68.48
Total	100.00		100.00			100.00

It was shown by local analysis that average size of Pd-containing cluster is in the range 15-20 nm.

3.2.4 Thermo-Programming Reduction and XAFS analysis

On the surface of Ni-Al membrane negligible amount of NiO was found (reduction area — 450°C, Fig.50) [39].
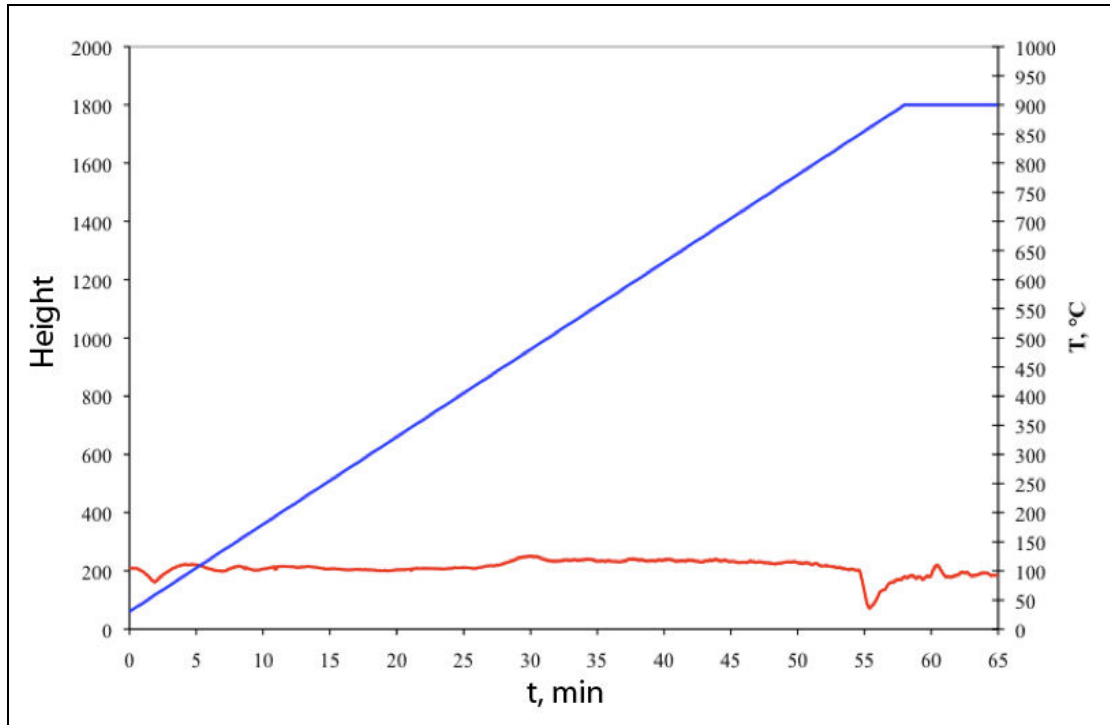
Fig.50. Thermo-reduction of Ni-Al membrane.

In the reduction spectrum of [La-Ce]-MgO-TiO$_2$/Ni-Al catalytic system there are three pronounced — one is at 450°C (NiO) and others are in the range of 700-900°C (CeO$_2$) (Fig.51) [40].
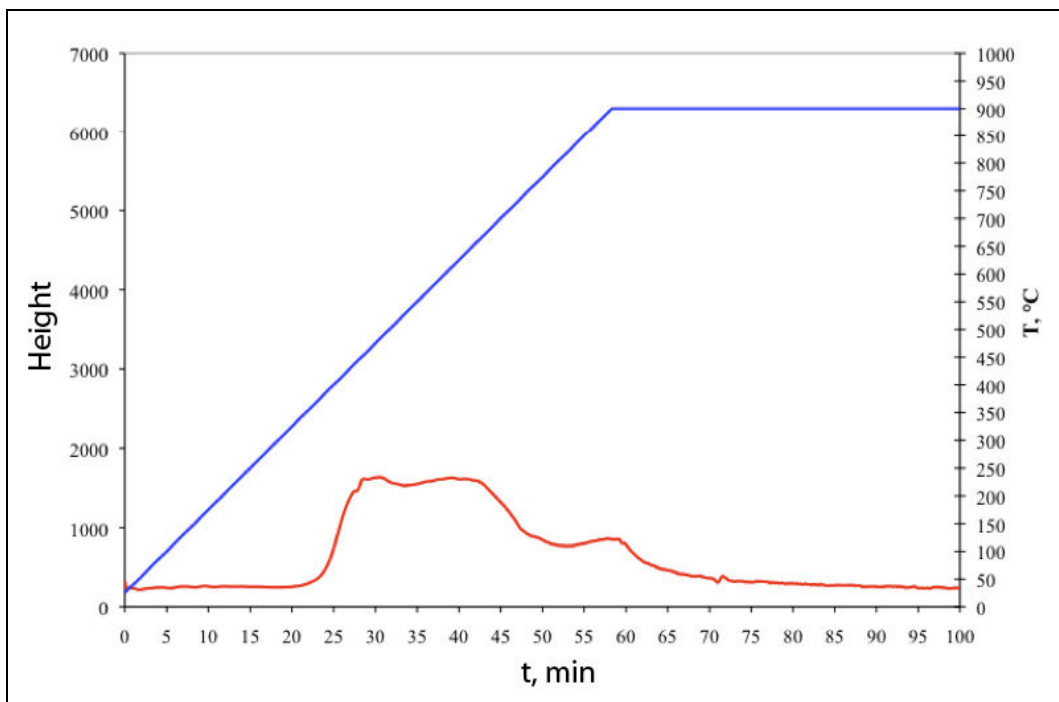
Fig.51. Thermo-reduction of [La-Ce]-MgO-TiO$_2$/Ni-Al membrane catalytic system.

The [Pd-Mn]-TiO$_2$/Ni-Al membrane catalytic system reducts strongly in the range of 350-650°C (NiO and PdO) [41] and a bit at high temperatures 750-900°C (Mn^{3+} into Mn^{2+}) (Fig.52) [42].
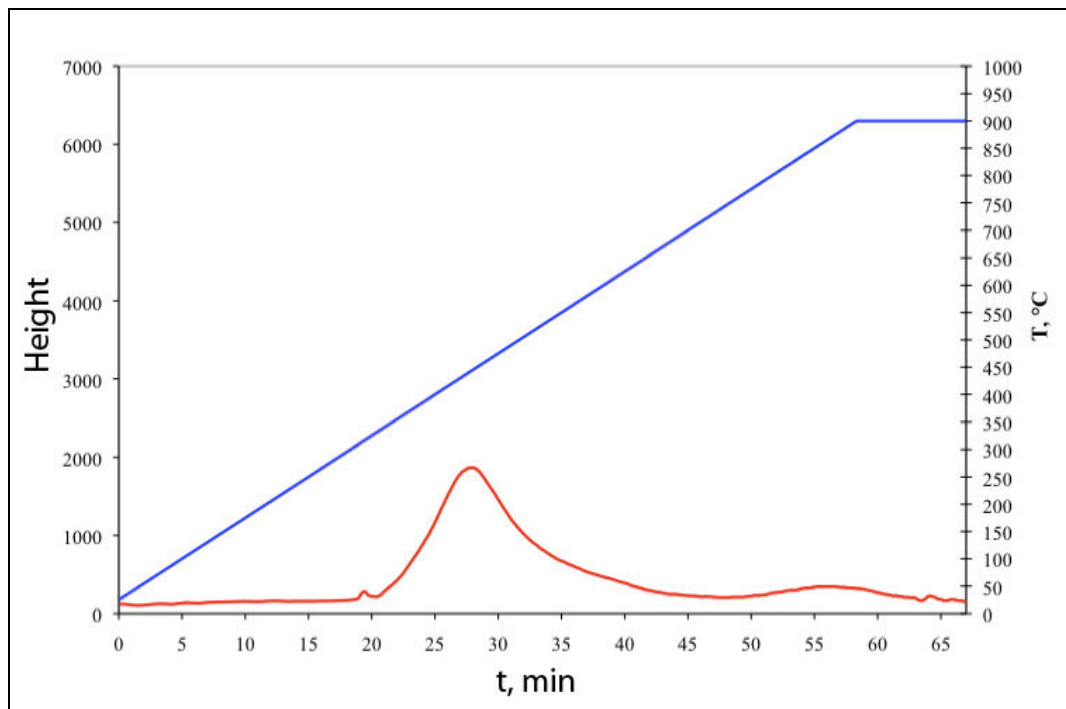
Fig.52. Thermo-reduction of [Pd-Mn]-TiO$_2$/Ni-Al membrane catalytic system.

These results were proved by XAFS. It was found that in initial Pd-Mn-containing membrane catalytic systems Pd is presented in its oxide phase of PdO, which reduces into Pd in the studied process. Manganese changes its oxidation level from Mn^{3+} to Mn^{2+}.

3.2.5 X-Ray Diffraction

By use of x-ray diffraction phase composition of membrane material was determined. It was found that it mostly consists of cubic AlNi$_3$ (d, A: 3.56; 2.52; 2.06; 1.78; 1.26; 1.08; 1.03) and Ni (d, A: 2.04; 1.77; 1.25; 1.07; 1.02), also the presence of nickel carbide (NiC) (d, A: 2.04; 1.77; 1.26; 1.07; 1.02) and carbon (C) (d, A: 2.04; 1.77; 1.25) are not inconceivable. Metal oxides of rare-earth metals, found by EDX, were not identified because of high phase dispersion (Fig.53).
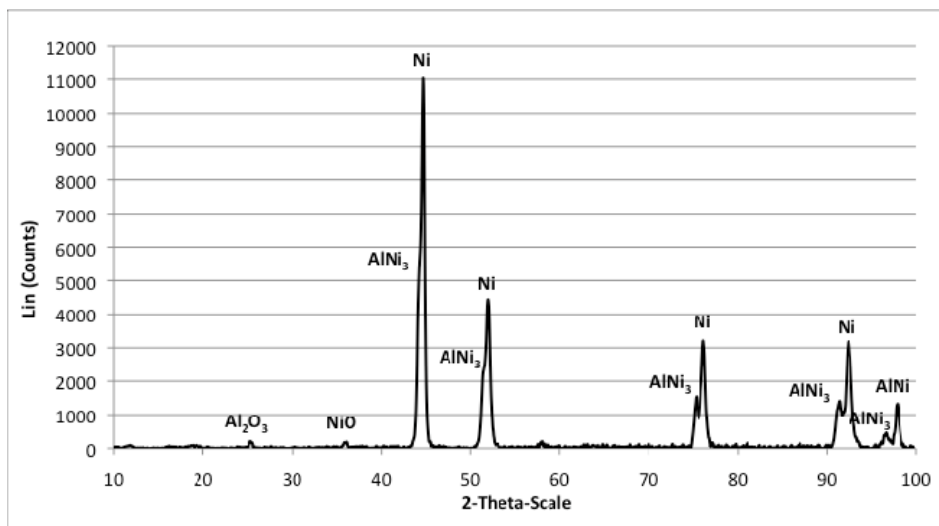
Fig.53. XRD of Ni-Al membrane.

In structures of modified membranes nickel mainly presents in the form of NiO (d, A: 2.41; 2.08; 1.47; 1.26; 1.20). Formation of structurized oxide phase must occur as a result of solid state phase transformations on the stage of catalyst preparation (Fig.54, 55).
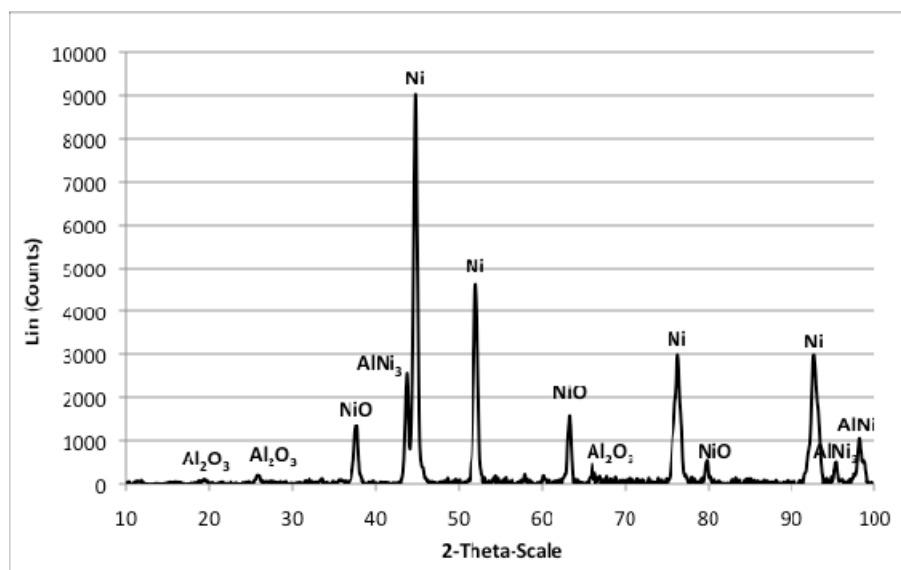
Fig.54. XRD of [La-Ce]-MgO-TiO$_2$/Ni-Al membrane catalytic system.
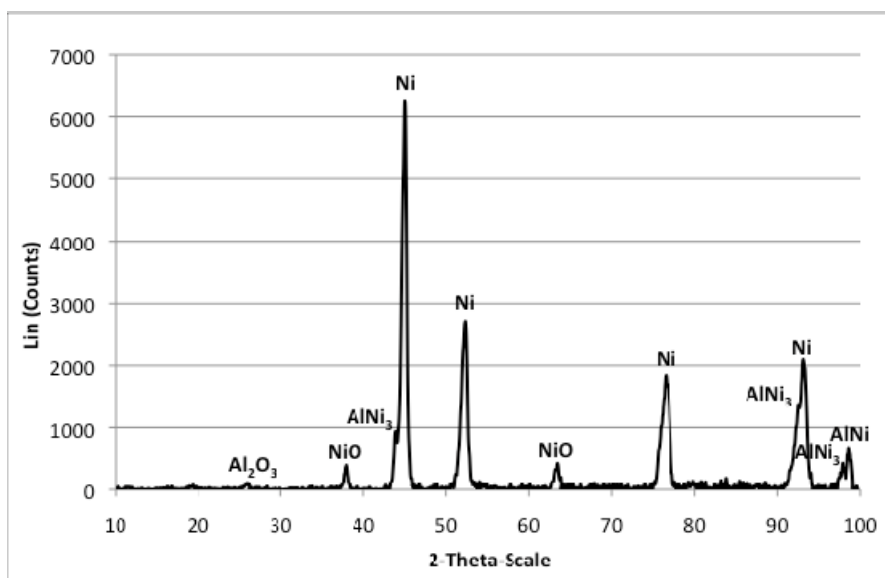
Fig.55. XRD of [Pd-Mn]-TiO$_2$/Ni-Al membrane catalytic system.

Surface oxide phases reduction capability of Ni-Al, [La-Ce]-MgO-TiO$_2$/Ni-Al and [Pd-Mn]-TiO$_2$/Ni-Al catalytic systems were studied by thermo-programming reduction method (TPR).

3.2.6 Helium Pycnometry

Physic density of membrane catalytic systems was determined by helium pycnometry method. It was found that material has a high-density; close to the density of nickel* (Table 6).

Table 6. Density of membrane catalytic systems

№	Sample	ρ, g/sm^3
1	Ni-Al	7.7292
2	[La-Ce]-MgO-TiO$_2$/Ni-Al	6.7155
3	[Pd-Mn]-TiO$_2$/Ni-Al	6.9982

*ρ(Ni) = 8,9020 g/sm^3

3.2.7 Mercury Porosimetry

It was proved by method of mercury porosimetry that application of small amount of catalyst on the membrane decreases pore diameter strongly (Table 7) that can be an

explanation of catalytic activity drastic rise in the context of stochastic collision theory. Open channels length decreasing of membranes points to increasing of their tortuosity.

Table 7. Average pore diameter and porosity of membrane catalytic systems.

№	Sample	Pore d_{median}, nm	Porosity, %	Channel lenght, mm
1	Ni-Al	224.9	38.0	0.3
2	[La-Ce]-MgO-TiO$_2$/Ni-Al	48.8	20.2	0.2
3	[Pd-Mn]-TiO$_2$/Ni-Al	88.0	12.9	0.2

3.2.8 Low-Temperature Nitrogen Sorbtiometry (BET)

Specific surface of membrane catalytic systems porous structure was determined by nitrogen sorbtiometry method (BET). It was found that ceramic membranes have relatively large (for metals) surface, which increase greatly after application of a small amount of catalyst. Data about sample specific surfaces is given in Table 8.

Table 8. Specific surfaces of membrane catalytic systems.

№	Sample	$S_{sp.}$, m^2/g
1	Ni-Al	0.08
2	[La-Ce]-MgO-TiO$_2$/Ni-Al	0.30
3	[Pd-Mn]-TiO$_2$/Ni-Al	0.16

As it was sited above, increase of specific surface can be an explanation of membrane catalytic systems high catalytic activity.

4. CONCLUSIONS

1.   Thermo stable membrane catalytic systems for dry reforming of methane and light hydrocarbons at temperatures up to 800°C are developed. On [La-Ce]-MgO-TiO_2/Ni-Al and Pd-Mn-TiO_2/Ni-Al systems in DMR process syngas productivities 10500 and 7500 l/h·$dm^3_{membr.}$ correspondingly, with syngas composition H_2/CO 0.63 – 1.25 and 50%-conversion of initial gas mix (CH_4/CO_2=1) were achieved.

2.   It was shown that rate of dry methane reforming on membrane catalytic systems with 0.008 — 0.055%$_{mass.}$ of catalytic components, applied to internal surface of membrane channels, more than in one order higher than rate of this process in a traditional reactor with a bulk layer of the same catalyst, that indicates intensification of heterogeneous catalytic processes on catalytic membranes. A non-additive effect of activity increase (in apr. 2 times) was found for mixture of Pd and Mn catalytic components.

3.   In the continuous DMR experiment was shown that membrane catalytic systems are stable in the process for a long time (40 h) without evident decrease in catalytic activity and selectivity.

4.   By SEM+EDX and TEM methods was identified that metal oxide catalytic components are distributed uniformly on the internal channels surface of membranes. It was shown that average sizes of La-Ce and Pd-containing catalytic clusters are about 15-20 nm. Structural oxygen of surface metal oxides, that initiates heterogeneous catalytic reactions in studied processes, was found. By XAFS and TPR methods was found that in initial Pd-Mn-containing membrane catalytic systems Pd is presented in its oxide phase of PdO, which reduces into Pd in the studied process. Manganese changes its oxidation level from Mn^{3+} to Mn^{2+}.

5.   Study of dry methane reforming dynamics on membrane catalytic systems has showed that the first stage initiates by methane oxidation by structural oxygen of surface metal oxides and CO_2 reacts with deposited high-dispersive carbon, which forms by methane dissociation, by reverse Bell-Boudoir reaction. Instead of direct reactions there are also a number of side, such and water-gas shift reaction and CO_2 hydrogenation that effect on process selectivity. Dynamics of DMR on porous membrane catalytic systems was studied. On the base of obtained data a mechanism of the process was proposed.

5. PROSPECTIVES

Recently great attention is given to use of porous ceramic membranes as carriers for high disperse catalytic components. Membrane-catalytic systems have more than 10^8 pores on 1 cm^2 of top-surface and can be considered as "ensemble" of nano-reactors. Some general advantages of micro reactors should be noted: compactness of industrial installations, easy scaling up of membrane unit, and good operation control of the process in the reactor. The most prospective trends in this field are syngas, light olefins and hydrogen production from natural gas and main renewable biomass products, such as methane, light hydrocarbons, alcohols and organic acids, as well as integration with solid oxide fuel cells.

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Autors contribution to experiments.

Experiment	Authors contribution, %	Institute
Dry reforming of methane and light hydrocarbons	100	TIPS RAS
Study of DRM dynamics	30*	ICP RAS
Synthesis of MCS	40	ISMAN RAS, TIPS RAS
Helium pyknometry	90	LSGC-ENSIC
Mercury porosimetry	50	LSGC-ENSIC
BET	70	LSGC-ENSIC, LMSPC-ECPM
SEM-EDX	90	LSGC-ENSIC, LMSPC-ECPM
TEM	90	LMSPC-ECPM

TPR	90	LMSPC-ECPM
XRD	90	LMSPC-ECPM
XAFS	20*	IC SO RAS

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ICP RAS – N.N Semenov Institute of Chemical Physics RAS, Moscow, Russia;

ISMAN RAS – Institute of Structural Macrokinetics and Problems of Material Sciences RAS, Chernogolovka, Russia;

IC SO RAS – G.K. Boreskov Institute of Catalysis SO RAS, Novosibirsk, Russia;

LSGC-ENSIC — Laboratoire des Sciences du Génie Chimique — Ecole nationale supérieure des industries chimiques, Nancy France;

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8. ACKNOWLEDGEMENTS

9. AUTORISATION DE SOUTENANCE

AUTORISATION DE SOUTENANCE DE THESE
DU DOCTORAT DE L'INSTITUT NATIONAL
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VU LES RAPPORTS ETABLIS PAR :
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Le Président de l'Institut National Polytechnique de Lorraine, autorise :

Monsieur FEDOTOV Alexey

à soutenir devant un jury de l'INSTITUT NATIONAL POLYTECHNIQUE DE LORRAINE,
une thèse intitulée :

« Conversion du méthane et du dioxyde de carbone avec des membranes catalytiques
poreuses »

en vue de l'obtention du titre de :

DOCTEUR DE L'INSTITUT NATIONAL POLYTECHNIQUE DE LORRAINE

Spécialité : « Génie des procédés et des produits »

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Le Président de l'I.N.P.L.,

F. LAURENT

Le Vice-Présidente
du Conseil d'Administration de l'INPL

Christine ROIZARD

10. SHORT ABSTRACT

CONVERSION DU METHANE ET DU DIOXYDE DE CARBONE SUR DES MEMBRANES POREUSES CATALYTIQUES, par Alexey S. FEDOTOV

Mots-clef : reformage à sec, membranes catalytiques, nanoréacteurs, valorisation de déchets

Résumé. L'étude concerne un nouveau procédé de reformage du gaz naturel en gaz de synthèse par le dioxyde de carbone (RSM), en vue de l'utilisation rationnelle des déchets carbonés industriels pour la production d'hydrocarbures et d'hydrogène. Cette méthode utilise des systèmes à membranes catalytiques inorganiques (SMC) qui favorisent des réactions catalytiques hétérogènes en phase gazeuse dans des micro-canaux céramiques. La surface active des catalyseurs formés à l'intérieur des canaux est faible en termes de superficie, mais elle est caractérisée par une valeur élevée du facteur Surface/Volume du catalyseur, qui induit une efficacité importante de la catalyse hétérogène.

Les SMC, formés à partir de dérivés alcoxy et des précurseurs métalliques complexes, contiennent de 0,008 à 0,055% en masse de nano-composants mono- et bimétalliques actifs répartis uniformément dans les canaux. Pour les systèmes [La-Ce]-MgO-TiO$_2$/Ni-Al et Pd-Mn-TiO$_2$/Ni-Al, les productivités de 10500 et 7500 l/h·dm^3$_{membr.}$ ont été respectivement obtenues lors du RSM dès 450°C avec une composition de gaz de synthèse H$_2$/CO allant de 0,63 à 1,25 et un taux de conversion de 50% de la charge CH$_4$/CO$_2$ (1/1). Ainsi les SMC sont d'un ordre de grandeur plus efficace qu'un réacteur à lit fixe du même catalyseur. Le RSM est initié par l'oxydation de CH4 par l'oxygène de structure des oxydes métalliques présents en surface, et le CO$_2$ réagit avec le carbone finement divisé provenant de la dissociation de CH$_4$. Une synergie catalytique a été mise en évidence pour le système Pd-Mn. Ces SMC de 10^8 pores par cm^2 de surface constituent un ensemble de nano réacteurs de fort potentiel industriel (synthèse d'oléfines, biomasse).

CONVERSIONS OF METHANE AND CARBON DIOXIDE ON POROUS CATALYTIC MEMBRANES, by Alexey S. FEDOTOV

Keywords: Dry reforming, catalytic membranes, nanoreactors, waste valorization

Abstract. This study reports the development of a new process to convert methane and carbon dioxide (dry methane reforming - DMR) into valuable products such as syngas from non-oil resources. The practical interest is to produce syngas from carbon containing exhaust industrial gases. This process uses membrane catalytic systems (MCS) that support heterogeneous catalytic reactions in gaseous phase in ceramic micro-channels. The active surface of the catalysts formed inside the micro-channels is low in term of area, but it is characterized by a high value of the catalyst surface/volume ratio, which induces a high efficiency of heterogeneous catalysis.

The SMC are formed from alkoxy derivatives and precursor metal complex containing between 0.008 and 0.055% by weight of nano-components mono-and bimetallic active distributed evenly in the channels. For systems [La-Ce] -MgO-TiO$_2$/Ni-Al and Pd-Mn-TiO$_2$/Ni-Al, productivities of 10500 and 7500 l/h · dm3 $_{membr.}$ were respectively obtained by RSM at 450°C with a composition of syngas H$_2$/CO ranging from 0.63 to 1.25 and a conversion rate of 50% with a CH$_4$/CO$_2$ (1/1) feed. Thus the CMS is an order of magnitude more efficient than a fixed bed reactor of the same catalyst. The MDR is initiated by the oxidation of CH$_4$ by structural oxygen of metal oxides available on the surface, and the CO$_2$ reacts with the finely divided carbon arising from the dissociation of CH$_4$. A catalytic synergy has been demonstrated for the system Pd-Mn. This CMS, having 10^8 pores per cm^2 of surface, can be considered as a set of nano reactors. Thus this new approach is very promising for industry (synthesis of olefins, uses of biomass).