Development of high-performance oxygen-conducting membranes and compact synthesis gas generators on their base

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This paper presents some results of research aimed at design of supported mixed –ionic-electronic conducting (MIEC) membranes for syngas generation by selective oxidation of the natural gas with oxygen transferred from the air through these membranes. This includes design of mechanically strong macroporous substrates made of refractory ceramics;   synthesis of complex MIEC perovskites (doped La nickelates, manganites, cobaltites-ferrites, gallates etc);   estimation of the mixed oxides ability to activate O_2 molecules and their lattice oxygen mobility; selection of catalysts able to efficiently convert methane into syngas by the lattice oxygen; supporting thin layers with a graded composition and porosity (including gas-tight one) on the substrate; testing of lab-scale membranes prototypes for the oxygen permeability and efficiency in syngas generation.

1. Introduction

Supported MIEC membranes are now considered as a promising option for generation of syngas by selective oxidation of hydrocarbons by oxygen separated from the air (Liu et al., 2006). However, design and manufacturing of these materials still present a demanding task requiring combined efforts of specialists in the fields of solid state chemistry/ionics, materials research and catalysis. This is caused by a high gradient of the oxygen chemical potential across the membrane thickness leading to materials degradation and/or mechanical failure/cracking in real high-temperature operation conditions. A possible solution is based upon the concept of functionally graded layers differing by the porosity and chemical composition consequently supported onto the macroporous "inert" substrate.

This paper presents results of testing of some basic concepts in design of multilayered functionally graded supported oxygen –conducting membranes using both refractory alloy or ceramic substrates and different MIEC materials with perovskite-like structure (gallates, cobaltites, ferites, nickelates etc) prepared via different routes (ceramic, mechanical activation, Pechini, sol-gel). Oxygen mobility estimated by the data of O_2 TPD and oxygen isotope exchange was used as one of the criteria for selection of materials for the air side of membrane. Efficiency in methane conversion into syngas

combined with reasonable phase stability in reducing conditions served as guidelines for selection of MIEC materials for the fuel side of membrane. As catalytic materials, ceria-zirconia solid solutions doped by La and promoted by Pt, Ru and/or $LaNiO_3$ were used (Sadykov et al., 2005a; Pavlova et al., 2004).

2. Experimental

2.1. Macroporous substrates

For manufacturing of macroporous substrate comprised of mullite- quartz glass composite, the clay-water slurries were prepared on the bases of available kaolins from Ukrainian and Russian deposits with addition of sodium electrolytes. Burning organic additives were added to slurry to increase an open porosity, while $Al(OH)_3$ (Gibbsite) powder comprised of 1-10 μm platelet-like particles was added to enhance the thermal stability. The green dead-end tubes obtained by casting of slurries into gypsum forms with subsequent drying were fired at T_g = 850 – 1000 °C before leaching. Leaching of macro-porous metakaolinite substrate was carried out in acid (pH~2) solutions to increase porosity and thermal stability at sintering temperature T_s. Metakaolinite was modified as well by alumina- or zirconia sols. A buffer interlayer was deposited onto porous dead-end tubes by ethanol-based slurry of α-Al_2O_3 (a mean particles size ~44 nm) and then pre-sintered at T_p = 950 – 1100 °C. The open porosity of supports was estimated from the water uptake (Zyryanov and Sadykov, 2006).

Macroporous planar stainless –steel substrates with the average pore size ~ 10 microns and porosity ~ 50 % (thickness 50-100 microns) were obtained from Russian sources.

As substrates, porous ceramics prepared from the$(La_{0.9}Sr_{0.1})(Ga_{0.7}Fe_{0.3})O_{3-y}$ (LSGF), and $(Sr_{1.8}La_{0.2})(GaFe)O_{5.1}$ (SLGF) powders were also tested as well. The poly(methyl methacrylate), used as a pore former, was added to the LSGM and SLGF powders which were pressed and then sintered at 1720 and 1420 K, respectively, with the intermediate step at 970 K to burn the pore former.

2.2. Preparation of complex perovskites and catalysts

Dispersed samples of complex $AA'BB'O_{3+x}$ perovskites (A=La, A'-Sr, B,B'= Mn, Fe, Co, Ni, Cu), doped $La_2Ni(Cu,Fe)O_{4+x}$ samples with K_2NiF_4 structure and doped ceria or ceria-zirconia samples were prepared by a polymerized complex precursor route and calcined at 500-700 °C for 4 h (Borchert et al., 2006). Porous Ce-Zr-La-O layer on the fuel side membrane was promoted by Pt (1.4 wt.%) via incipient wetness impregnation with H_2PtCl_6 solution followed by drying and calcination at 700 °C.

For preparation of single-phase powders with fluorite or perovskite structure using mechanochemical activation route, mixtures of oxides were milled in a high energy planetary mill AGO-2 for 20–30 min (Zyryanov et al, 2005).

Complex gallates with perovskite and brownmillerite structures were prepared in forms of powders and ceramics via sol-gel route from water solutions of acetate and/or nitrate salts (Kaleva et al, 2006).

For preparation of films, suspensions of powders in organic solvents (ethanol, terpineol etc) with addition of some binders and plasticizer were used. For tubular substrates, films were consecutively supported onto the internal tube surface

2.3. Characterization of MIEC materials and membranes

Phase characterization was carried out by XRD using Cu K_α radiation. The data were collected in the 2θ range 10– 80° with a step 0.01, peaks being approximated by the Lorenzian shape. The X-ray particle size was estimated using the Scherrer equation.

The total electric conductivity of samples was measured in air at temperatures ranging from 300 to 1000 K using a 4284 A Precision LCR Meter.

EM images were recorded by a Tesla BS-350 SEM and a JEOL JEM-2010 TEM operating at 200 kV.

Dynamic isotope oxygen exchange was carried out in a static installation with MS control in the temperature-programmed mode (Sadykov et al, 2005b).

For samples pretreated in O_2 at 500 °C, oxygen temperature-programmed desorption into the stream of He and surface/bulk oxygen reactivity by CH_4 temperature-programmed reduction (TPR, 1% in He, ramp 5°/min from 25 up to 880 °C) were studied in flow kinetic installations (Sadykov et al., 2005a).

Catalytic activity of powdered samples was studied in a flow installation with 1% CH_4+ 0.5% O_2 feed as described earlier (Sadykov et al., 2005). Tubular membrane reactors were tested with supply of CH_4 in He feed through the quartz tube inserted into the dead-end membrane with hermetic sealing of cool ends.

3. Results and discussion

3.1. Composite ceramic substrates

The typical view of functionally-graded membrane reactors (CMR) is shown in Fig. 1. The thickness of substrate (open porosity up to 50%) is ~1 mm (Fig. 2), 1st ceramic layer ~60 μm, 2nd layer ~30 μm, 3rd layer ~15 μm, 4th layer ~5 μm, protective 5th layer ~2 μm, composition of MIEC layers being earlier described in details (Zyryanov et al., 2005). A buffer α-Al_2O_3 interlayer is introduced to prevent too strong chemical reaction between MIEC ceramics and silica glass of substrate. A top protective layer of MIEC membrane is comprised of $Ce_{0.8}Gd_{0.2}O_{2-x}$ + $LaMnO_3$ composite ensuring an enhanced stability at a feed side relative to single phase perovskites.

3.2. Complex MIEC perovskites

Complex nickelates and cobaltites

According to TEM and XRD data, samples of $La_{1-x}Sr_xMe^1_{1-y}Me^2_yO_{3+x}$ perovskites prepared via Pechini or mechanochemical activation route are single-phase
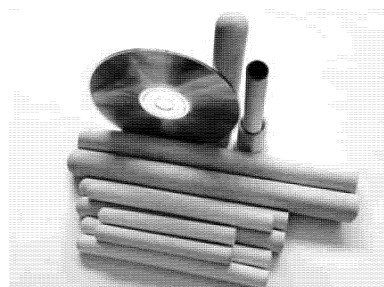

Fig. 1. Porous tubular/dead-end tubular supports and CMR obtained by casting technology.
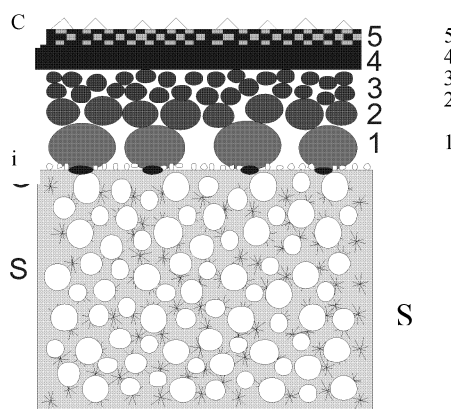

Fig. 2. A scheme of multilayered membrane. S- macroporous substrate, i- buffer interlayer, C- finely dispersed catalyst, 1-3 porous MIEC ceramic layers, 4- dense MIEC ceramic layer, 5- protective MIEC composite layer.

nanocrystalline materials (Zyryanov et al., 2005; Borchert et al, 2006). The total conductivity level at 500-800 K for these perovskites followed the well-known order Ni>Co>Mn. The highest level of the total conductivity ($\sim 10^3$ S/cm) was revealed for $La_{0.8}Sr_{0.2}Ni_{0.4}Fe_{0.6}O_{3+x}$ sample. For non-stoichiometric nickelate $(La_{0.8}Sr_{0.2})_2Ni_{0.8}Fe_{0.32}O_{4+x}$ of A_2BO_{4+x} type, conductivity is below 10 S/cm.

Oxygen desorption starts from ~ 150 ^0C for cobaltites, from $\sim 250\text{-}300$ ^oC for ferrites and nickelates, and from ~ 500 ^oC for manganites. In dynamic experiments, oxygen exchange starts at $\sim 250^0C$ for cobaltites, at $\sim 300^0$ C for nickelates, and at $\sim 500^0C$ for manganites. At intermediate temperatures (~ 550 ^oC) the rate of heteroexchange ($\sim 10^{17}$ molec. O_2/m^2s at 4 Torr O_2) is the highest for pure $LaMnO_{3+x}$ due to a weak oxygen bonding with Mn^{4+} cations. Close values of the rate of heteroexchange R (lgR varies in the range of 16.4-16.8 at 550 ^oC, 4 Torr O_2) were obtained for complex perovskites containing Fe, Ni or Co cations or even for pure La_2NiO_4 sample with two-dimensional K_2NiF_4-type structure. On the other hand, for $LaMnO_{3+x}$ perovskite, the lattice oxygen mobility characterized by the dynamic degree of exchange (Sadykov et al., 2005b) is quite low (~ 1 monolayer at 500-600 ^oC) due to well-known absence of oxygen vacancies in the lattice. On contrary, for La_2NiO_4, dynamic degree of exchange (~ 13 monolayers) is much higher. This means that the lattice oxygen mobility in this sample controlled by the interstitial oxygen (Liu et al., 2006) is indeed very high. For more complex $La_{0.8}Sr_{0.2}Ni_{0.4}Fe_{0.6}O_{3+x}$.sample, dynamic degree of the oxygen exchange is only slightly higher (~ 16 monolayers) correlating, perhaps, with a higher total conductivity. It is quite interesting that dynamic degree of the oxygen exchange for complex nickelates is even higher than that for $La_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_3$ sample (~ 11.5 monolayers) known as the best MIEC system. A low thermal expansion coefficient for nickelates ($\sim 11\text{-}16x$ 10^{-6} by Nie at al., 2006) makes them especially attractive due to a good compatibility with macroporous ceramic supports.

In CH_4 TPR experiments, reduction of complex nickelates starts at ~ 600 ^oC yielding mainly syngas, thus demonstrating a high reactivity and syngas selectivity of the lattice oxygen of these systems. At ~ 700 ^oC, for these systems, in CH_4 +O_2 feed even at very short (5 ms) contact times, 50-80 % of methane was converted into syngas, and no performance deterioration due to coking was observed. Hence, complex nickelates doped with Sr and Fe could also be used as MIEC components and catalysts for the fuel side of membrane.

Complex gallates

The highest ionic conductivity was revealed in ceramics of $(La_{0.9}Sr_{0.1})(Ga_{0.8}Mg_{0.2})O_{2.85}$ composition. Formation of solid solutions on the bases of this composition $(La_{0.9}Sr_{0.1})[Ga_{1-x}Me_x)_{0.8}Mg_{0.2}]O_{3-y}$ with Me=Fe, Ni, Mn, Cr and brownmillerite ceramics $(La_{0.2}Sr_{1.8})[Ga(Fe_{1-x}Mg_x)]O_{5-z}$ with $x=0-0.5$ was studied in details (Politova et al, 2004; Politova et al., 2005; Politova et al., 2006). The most uniform sols were formed in the case of perovskite LSGF composition, and the pure perovskite phase formation was observed at calcination temperatures as low as 570 K. For the brownmillerite SLGF composition, precipitation by ammonia resulted in the suspension formation. X-ray diffraction patterns confirmed the appearance of the brownmillerite structure phase at 870 K which formed completely at 1070-1370 K.

The correlation between composition, conductivity and oxygen permeation characteristics was revealed. The oxygen permeability reaches its maximum values in perovskite compositions with $x\sim0.3$. The highest oxygen permeability values $J > 0.1$ $cm^3/cm^2 \cdot min$ were measured for iron-containing perovskite and brownmillerite structure compositions at temperatures $\sim 1000^oC$ (Fig. 3).
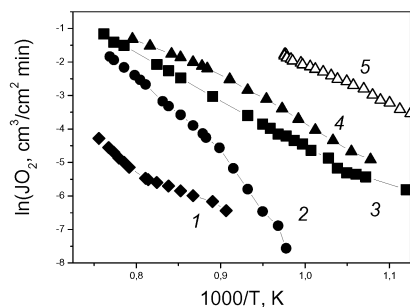
Fig. 3.Temperature dependencies of oxygen permeability of perovskite ceramics $(La_{0.9}Sr_{0.1})[Ga_{1-x}Me_x)_{0.8}Mg_{0.2}]O_{3-y}$ with $x=0.3$, $Me=Cr$ (1), Ni (2), Fe (3) and brownmillerite ceramics $(La_{0.2}Sr_{1.8})[Ga(Fe_{1-x}Mg_x)]O_{5-z}$ with $x=0$ (4), 0.2 (5). Samples thickness 1 mm, working surface 6.5-7 mm^2.
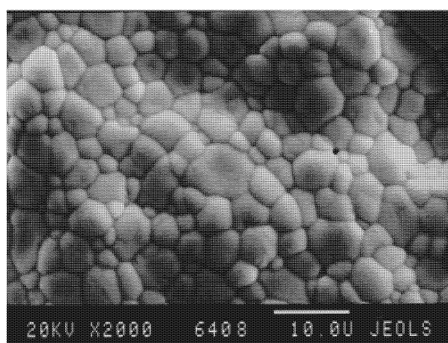
Fig. 4. SEM micrographs of the $(Sr_{1.8}La_{0.2})(GaFe)O_{5.1}$ films on porous substrates of the same composition. The powders used were prepared by the sol-gel method

The results obtained support the conclusion that the lanthanum gallate–based compositions may be used for the development of membrane materials only in the form of layers about 10-100 μm thick on porous substrates.

The powders prepared were used for deposition of slurries on various porous substrates. It is worth to note that the pure perovskite phase dense films were obtained on porous stainless steel only if the sintering was carried out in a reducing atmosphere containing mixture of He and CH_4 with the ratio 95:5 vol. %, respectively.

Films with green thickness of 40 μm deposited on ceramic porous substrates and annealed at 1320 – 1340 K were dense without cracks or holes (Fig. 4). According to the gas tightness tests performed by the GC detection of N_2 at the effluent side of a membrane, the tight films were obtained only for the SLGF films on porous SLGF substrates.

Hence, a principal possibility of obtaining dense MIEC gallates layers on porous layers of the same materials is demonstrated. With a due regard for instability of gallates in strongly reducing conditions due to metallic Ga evaporation, gallate layers are to be covered by more stable in reducing conditions composites such as composites of complex nickelates, manganites etc with doped ceria (Zyryanov et al, 2005).

3.3. Performance of catalytic membrane reactors

A lot of catalytic membrane reactors on macroporous ceramic substrates were prepared supporting layers with graded porosity and composition (complex perovskites or their composites with ceria-based fluorite-like complex oxides) as described by Zyryanov et al. (2005) in details for the case of macroporous perovskite substrate. Preliminary results of tests in the partial oxidation of methane were obtained for gas-tight reactors with nonselective room temperature air leakage into He stream < 1%. As a rule, tests show a relatively low (5-10%) syngas selectivity, especially for reactors with the top layer comprised of LSGM-based perovskites. Rather good results were obtained for reactors with protective layers comprised of Gd-doped ceria + $LaMnO_3$ composites covered by porous layer of $Pt/Ce_{0.4}Zr_{0.4}La_{0.2}O_{2-x}$. catalyst. A microspherical $Pt/LaNiO_3/Ce_{0.4}Zr_{0.4}La_{0.2}O_{2-x}/\gamma\text{-}Al_2O_3$ catalyst (Pavlova et al, 2004) loaded into the CMR strongly improved performance increasing methane conversion at 880 $^{\circ}C$ up to 70 % with

syngas selectivity up to 90% . The optimization of CMR including variation of compositions of consecutive layers, catalysts and procedures of their deposition in multilayered membranes is in progress.

4. Conclusions

Basic approaches to design of multilayered catalytically active MIEC membranes for syngas generation by partial oxidation of syngas are verified. This includes design of original macroporous tubular membrane substrate comprised of mullite-quartz glass composite; development of procedures for preparation of nanocrystalline easily sintering complex perovskites and their supporting as layers with varying porosity and composition on macroporous substrates; selection of the most promising compositions of consecutively supported layers possessing required mobility and reactivity of the lattice oxygen. Preliminary tests of CMR demonstrated reasonably good methane conversion and syngas selectivity for some configurations of layers.

5. Acknowledgements

6. References

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