

NEW NANOSTRUCTURED PEROVSKITE-TYPE CATALYSTS FOR LIGHT OLEFINS PRODUCTION

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Abstract

Perovskite-type structures with mixed oxygen-ionic and electronic conductivity, high activity and stability are used as catalysts for high temperature processes such as synthesis gas production and ethylene and propylene subsequent synthesis. The nanostructured perovskite-type oxides $GdFe_{1-x}Mn_xO_3$ ($x = 0, 0.01, 0.05, 0.2, 0.5, 0.8$ and 1) were synthesized by ceramic and sol-gel technologies and were studied as catalysts for dry reforming of methane and the CO hydrogenation. The complex of physico-chemical investigation methods showed that samples obtained by sol-gel technology are in nanocrystalline state and these have a porous structure, and oxides prepared by ceramic technology are in sub-microcrystalline state. The sol-gel method makes it possible to obtain samples with higher catalytic performances in comparison with ceramic systems. Doping the B-site of gadolinium ferrites with manganese, and also surface modification with Mn leads to an increase in olefin selectivity over the entire temperature range. The highest stability, catalytic activity, and unsaturated hydrocarbons (ethylene and propylene) selectivity in the carbon oxides hydrogenation were observed over $GdFeO_3$, $GdFe_{0.95}Mn_{0.05}O_3$, 5 %wt Mn/ $GdFeO_3$ samples. It was established that the phase composition of all ferrites remains unchanged after catalytic reactions. Partial decomposition of catalysts and significant changes in the samples morphology didn't occur. Carbon is present on the used catalysts surface, but since the catalysts activity didn't change in repeated experiments for a long time, it is suggested that this carbon is mostly active. And formation of inactive carbon for samples obtained by sol-gel method is minimal.

Keywords: Carbon monoxide, reforming, Gd-Mn-Fe perovskite oxide, hydrogenation, methane, light olefins

1. INTRODUCTION

At present in the oil processing there is a steady increase of interest in alternative methods for synthesis gas producing, which plays an important role for the motor fuels production and in other chemical processes, particularly, to obtain ethylene and propylene is an important raw material for the chemical industry. Supported catalysts that contain metals of the Pt or Co, Ni, Fe subgroup are effective catalysts in the GTO (Gas to Olefins) processes, but the main drawback of these samples is related to both the high cost and the tendency to poison. In addition, using traditional catalysts, the products range is very wide. Therefore, the creation of effective catalysts with a predictable distribution of products and resistant to coking is a priority. In recent years, much attention has been paid to complex oxides with a perovskite-type structure, which have mixed oxygen-ion and electronic conductivity. A considerable amount of research indicates their high catalytic activity and selectivity, stability and low coking [1-4].

The aim of this work was to study the properties of nanostructured perovskite-type oxides $GdFe_{1-x}Mn_xO_3$ ($x = 0, 0.01, 0.05, 0.2, 0.5, 0.8$ and 1) in GTO processes (dry reforming of methane and carbon monoxide hydrogenation), and also the effect of preparation method and composition of complex oxides on their catalytic activity and selectivity.

2. EXPERIMENTAL

Nanostructured perovskite-type ferrites $\text{GdFe}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0, 0.01, 0.05, 0.2, 0.5, 0.8$ and 1) synthesized by sol-gel and ceramic technologies according to the procedures described in [5] were used as catalysts of dry reforming of methane (DRM) and carbon monoxide hydrogenation.

The manganese modification of the GdFeO_3 oxide surface was carried out by the multilayer impregnation method; the applied component amount was $1.0\text{-}5.0 \pm 0.5\%$ by weight of the carrier mass. The active component (Mn) was introduced onto a "base" carrier, which was selected as GdFeO_3 , by immersing it in a manganese nitrate salt solution. After impregnation, the solid was dried at $150\text{ }^\circ\text{C}$ for 3 hours and calcined at $450\text{ }^\circ\text{C}$ for 4 hours to form an oxide perovskite structure on the surface.

The results from synthesis were monitored via X-ray diffraction (XRD). ARL X'TRA and Rigaku MiniFlex II diffractometers with $\text{CuK}\alpha$ radiation were used to conduct our XRD experiments. A PDF2 database was used for phase identification. The size of coherent scattering region was estimated using Scherrer's equation.

Sample images were taken with a Zeiss EVO.40 scanning electron microscope at an accelerating voltage of 10 kV and a resolution of 3 nm (the microscope operated under low vacuum and did not require sputtering for nonconductive samples), and a Carl Zeiss Supra 40VP electron microscope at a voltage of 20 kV and a resolution of 1.3 nm.

Photon correlation spectroscopy using a Malvern Zetasizer Nano analyzer with 4 mW helium-neon laser (wavelength, 633 nm) was also used to determine particle size.

The catalytic activity in the DRM reaction was determined by supplying a reaction mixture with component ratio $[\text{CO}_2 : \text{CH}_4] = 1 : 1$. In the hydrogenation reaction, the ratios were $[\text{CO} : \text{H}_2] = 1 : 1; 1 : 2; 1 : 4$. Our experiments were conducted in flow catalytic reactors at atmospheric pressure and volumetric feeding rates of $0.5\text{-}1.0\text{ L/h}$ in the temperature range of $300\text{-}723\text{ K}$ (for hydrogenation) and $773\text{-}1223\text{ K}$ (for DRM). Products were analyzed on Crystal 2000M and Crystal 5000 chromatographs using a stainless steel column packed with porapak Q at 393 K , along with thermal conductivity and flame ionization detectors linked in sequence. The rate of formation of reaction products W ($\text{mol/h}\cdot\text{g}_{\text{cat}}$) and the specific catalytic activity (SCA) were measured after the system reached an equilibrium state, estimated from the invariability of the chromatographic peaks and the normalized per unit mass of the catalyst

3. RESULTS AND DISCUSSION

The studied ferrites are classified as Ruddlesden-Popper phases [6,7]. The complex oxide GdFeO_3 is described as an oxide with a distorted perovskite structure in the literature [8].

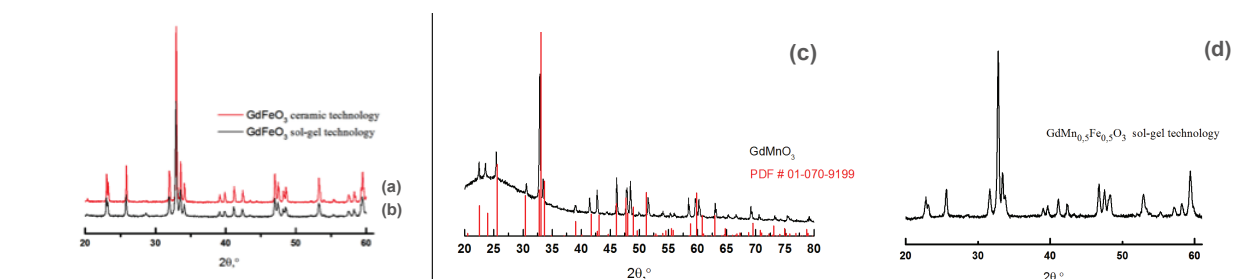


Figure 1 Diffractograms of complex ferrites GdFeO_3 : (a) ceramic technology; (b) sol-gel technology; GdMnO_3 (c), sol-gel technology; $\text{GdMn}_{0.5}\text{Fe}_{0.5}\text{O}_3$ (d), sol-gel technology

Using X-ray analysis, one phase with a perovskite-like layered structure was found in $\text{GdFe}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0, 0.01, 0.05, 0.2, 0.5, 0.8$ and 1) prepared via both the solid-phase and the sol-gel techniques (**Figure 1**). A comparison of the diffraction reflections and the determination of coherent scattering region (CSR) showed the

particles of the polycrystalline samples prepared using ceramic technology to be bigger than those of the same compound obtained with the sol-gel method.

According to photon correlation spectroscopy and scanning electron microscopy data (**Figure 2**), the particles were anisotropic, and the average diameter and length of the crystallites synthesized according to the ceramic technique were 2-10 and 10 μm , respectively. For the sol-gel products, these parameters were 30-60 and 200 nm, respectively. It should be noted that the particle morphology also differed: the shape of the particles prepared via the sol-gel method was uniform, as was the particle size distribution. In addition, the samples all had porous surfaces.

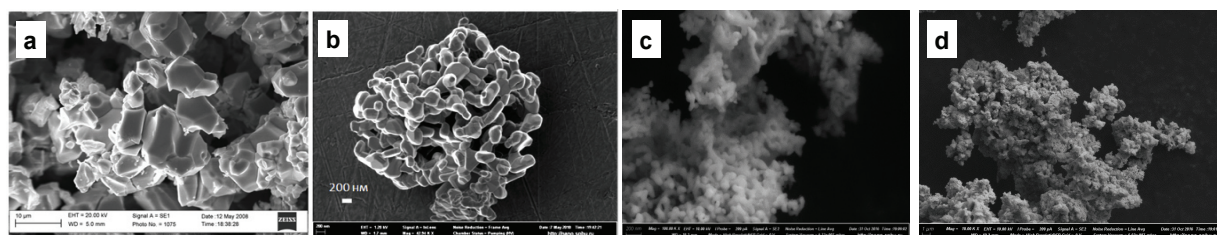


Figure 2 SEM images of complex layered oxide GdFeO_3 , prepared via ceramic technology (a) and the sol-gel method (b), GdMnO_3 (c), $\text{GdMn}_{0.5}\text{Fe}_{0.5}\text{O}_3$ (d)

According to the Mössbauer spectroscopy data, the iron atoms in the complex ferrites prepared using ceramic technology were in a magnetically ordered state, Fe^{3+} . Mössbauer spectra of the solid solutions synthesized via sol-gel technology showed the iron atoms in the GdFeO_3 samples to be in state Fe^{3+} in two fields with different symmetry.

During the DRM reaction over $\text{GdFe}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0, 0.01, 0.05, 0.2, 0.5, 0.8$ and 1) complex oxides up to 1000 K, the conversion of methane and carbon dioxide didn't exceed 10 and 20%, respectively. A further rise of temperature led to an increase in the process rate and at $T = 1223$ K the methane and carbon dioxide conversion to carbon monoxide and hydrogen amounted to 20 to 60%, depending on the perovskite composition (**Figure 3**) and the amount of CO being 2-3 times greater amount of hydrogen (**Table 1**).

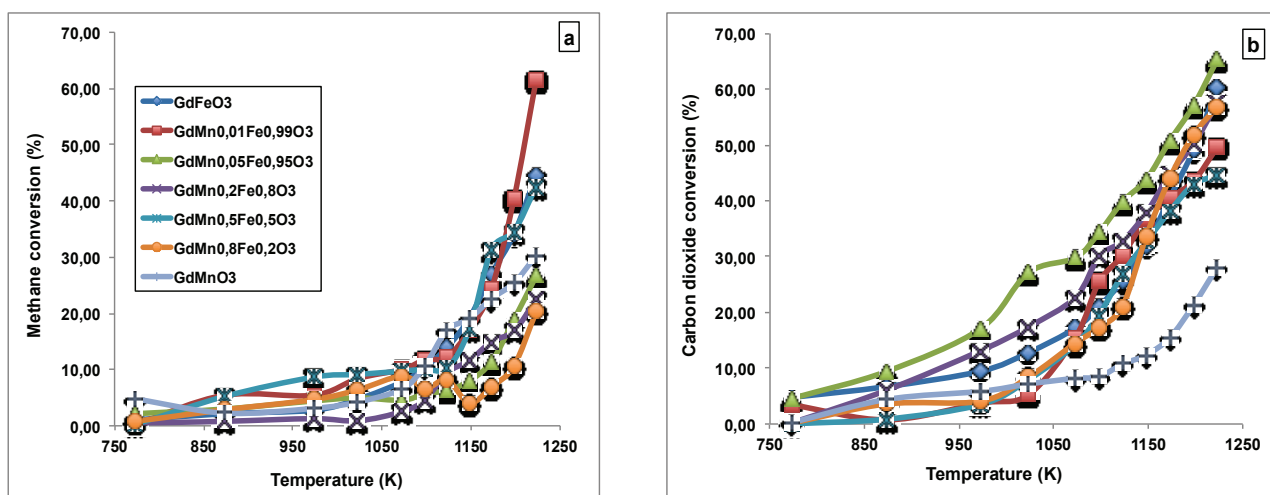


Figure 3 The temperature dependence of the (a) CH_4 and (b) CO_2 conversions

The manganese proportion increasing in the B-site of complex oxide led to a drop in activity in the high temperatures range. However, despite the low values of products formation rates, the highest hydrogen selectivity of 81% was achieved on the sample with $x = 0.2$ (**Table 1**).

In order to estimate the values of the efficient activation energies and the number of active surface centers of the investigated ferrites, the experimental data were processed in linear coordinates of the Arrhenius equation. The values of the hydrogen formation activation energies and the respective logarithms of the pre-exponential factors for the samples are presented in **Table 1**.

Table 1 Catalytic performances of $\text{GdFe}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0, 0.01, 0.05, 0.2, 0.5, 0.8$ and 1) ferrites for DRM process

Sample	α (CH ₄), %	α (CO ₂), %	W (CO), mol/(h*g)	W (H ₂), mol/(h*g)	S(CO), %	S(H ₂), %	E _a (H ₂) kDj/mol	ln k ₀
GdFeO ₃ (s-g)	45	60	0.212	0.128	80	56	198	19.3
GdMn _{0.01} Fe _{0.99} O ₃ (s-g)	62	50	0.223	0.110	80	35	177	15.1
GdMn _{0.05} Fe _{0.95} O ₃ (s-g)	27	65	0.133	0.074	67	66	195	16.4
GdMn _{0.2} Fe _{0.8} O ₃ (s-g)	22	58	0.155	0.080	88	81	176	17.4
GdMn _{0.5} Fe _{0.5} O ₃ (s-g)	43	45	0.127	0.042	74	28	178	14.2
GdMn _{0.8} Fe _{0.2} O ₃ (s-g)	20	57	0.147	0.069	88	77	169	16.5
GdMnO ₃ (s-g)	30	28	0.103	0.026	81	19	142	10.3

It can be seen that the manganese introduction into the anionic sublattice of ferrite leads to a decrease in the H₂ formation activation energy, as well as the corresponding lnk₀ values characterizing the number of active sites. For a sample with $x = 0.2$, the number of these centers turned out to be comparable with the initial ferrite, indicating a synergistic effect.

When carrying out reaction of carbon monoxide hydrogenation at the ratio of CO:H₂ = 1:2 over the GdMnO₃ and GdFeO₃ samples showed that the reaction products were the C₁-C₅ hydrocarbons. However, the amount of methane formed over GdMnO₃ was significantly less than over GdFeO₃ in the entire temperature range (**Figure 4a**).

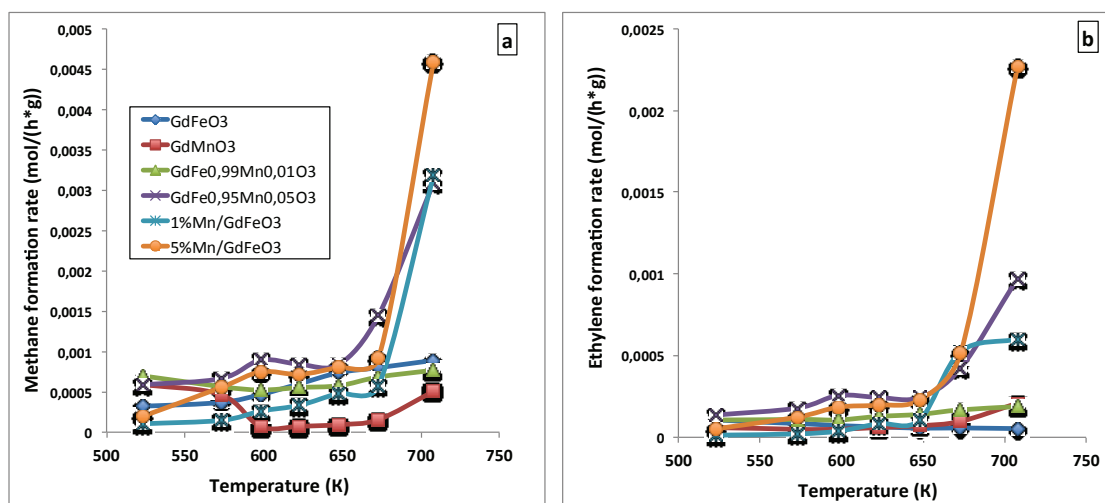


Figure 4 Temperature dependencies of the (a) methane and (b) ethylene formation rates at the ratio CO:H₂ = 1:2

A similar trend was observed in the ethylene formation (**Figure 4b**). The complete replacement of iron with manganese in the B-site in the ABO₃ perovskite structure resulted in an almost twofold increase in olefins selectivity (**Figure 5**). Changes in the qualitative composition of the products (hydrocarbons C₁-C₅) during the carbon monoxide hydrogenation on samples in which iron in the B-site was partially replaced by Mn (1% and

5%) were not observed. The increase of manganese proportion to 5% both in B-site of perovskite structure and on the surface led to increase in the products formation rates.

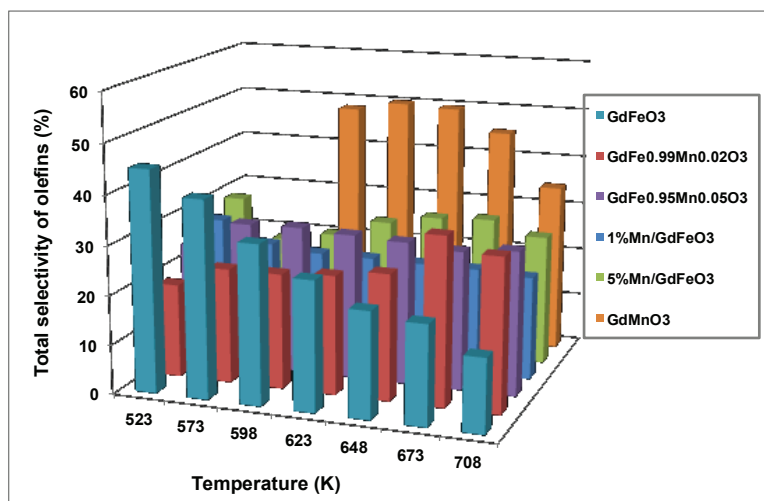


Figure 5 Temperature dependence of the all selectivities toward olefins at the ratio CO:H₂ = 1:2

The calculation of selectivities to ethylene and propylene showed that due to the suppression of methane formation when manganese is introduced into the gadolinium ferrite, the values of *S* significantly increase (**Figure 5**). Thus, the substitution of 1% Fe to Mn led to an increase in selectivity by the 1.5 times, and the replacement of 5% Fe by almost 2 times. We can assert about the emergence of synergetic effect in the iron and manganese action. It can be seen that the *S* values increase with the manganese content regardless of the modification method: the selectivities for samples containing 1% manganese on the surface are comparable with the selectivities for the sample with 1% manganese in the B-site of the complex oxide. A similar trend was observed for samples containing 5% manganese. At the same time, the influence of manganese in the anionic sublattice was stronger. The calculated apparent activation energies and logarithms of the pre-exponential factor for manganese modified samples are summarized in **Table 2**. A comparison of the data showed that the decrease of methane formation rates for samples with manganese in the B-site of the complex oxide is due to the energy factor (the increase in *E_a*), and the increase in selectivity to olefins is a frequency factor (a significant increase in $\ln K_0(\text{C}_2\text{H}_4)$). Doping the surface of oxides with manganese, on the contrary, leads to a decrease in the number of active centers responsible for the CH₄ formation and an increase in the number of centers on which ethylene is formed.

Table 2 Activation energies of methane and ethylene formation and logarithms of pre-exponential factors for GdFe_{1-x}Mn_xO₃ (*x* = 0; 0.01; 0.05 and 1) and Mn/GdFeO₃ samples for carbon monoxide hydrogenation

Sample	<i>E_a</i> (CH ₄), kDj/mol	$\ln K_0(\text{CH}_4)$	<i>E_a</i> (C ₂ H ₄), kDj/mol	$\ln K_0(\text{C}_2\text{H}_4)$
GdFeO ₃	48.0	3.60	72.0	7.40
1%Mn/GdFeO ₃	36.5	-0.90	70.9	4.12
5%Mn/GdFeO ₃	43.4	1.87	74.7	6.55
GdFe _{0.99} Mn _{0.01} O ₃	83.8	8.89	89.9	8.74
GdFe _{0.95} Mn _{0.05} O ₃	82.8	8.28	88.4	8.07
GdMnO ₃	51.3	0.36	29.3	-4.04

All the tested ferrites showed a high stability. It was established that the phase composition of all ferrites remains unchanged after catalytic reactions. Partial decomposition of catalysts and significant changes in the samples morphology didn't occur. Catalytic characteristics were preserved during the repeated experiments and were not changed after 50 hours of the experiment. The mass change of the catalyst after completion of all tests did not exceed 1% for all investigated systems. It may indicate a slight carbonization surface of the tested ferrites and the potential use for their further studies.

4. CONCLUSION

Physicochemical and catalytic properties of nanostructured perovskite-type oxides $GdFe_{1-x}Mn_xO_3$ ($x = 0, 0.01, 0.05, 0.2, 0.5, 0.8$ and 1) were synthesized and studied. A correlation between the preparation method, the composition and the structure of oxides, and their catalytic properties was established. It is shown that the hydrogen selectivity for dry reforming of methane depends on the manganese proportion in the layered oxide. Doping the anionic sublattice of gadolinium ferrites with manganese, and also surface modification with Mn leads to an increase in olefin selectivity for hydrogenation processes over the entire temperature range, which is associated with the appearance of a synergetic effect.

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REFERENCES

- [1] S.A. HOSSEINI, A. NIAEI, D. SALARI, M.C. ALVAREZ-GALVAN, J.L.G. FIERRO Study of correlation between activity and structural properties of Cu-(Cr, Mn and Co)₂ nano mixed oxides in VOC combustion. *Ceramics International*, 2014, no. 40, pp. 6157 - 6163.
- [2] ZAGAYNOV I.V., LOKTEV A.S., ARASHANOVA A.L., IVANOV V.K., DEDOV A.G., MOISEEV I.I. Ni(Co)-Gd_{0.1}Ti_{0.1}Zr_{0.1}Ce_{0.7}O₂ mesoporous materials in partial oxidation and dry reforming of methane into synthesis gas. *Chemical Engineering Journal*, 2016, vol. 290, pp.193 - 200.
- [3] BENEDETTA DE CAPRARIIS, PAOLO DE FILIPPIS, VINCENZO PALMA, ANTONIETTA PETRULLO, ANTONIO RICCA, CONCETTA RUOCCO, MARCO SCARSELLA Rh, Ru and Pt ternary perovskites type oxides BaZr_(1-x)Me_xO₃ for methane dry reforming. *Applied Catalysis A: General*, 2016, vol. 517, pp. 47-55.
- [4] KUN ZHAO, FANG HE, ZHEN HUANG, GUOQIANG WEI, ANQING ZHENG, HAIBIN LI, ZENGLI ZHAO. Perovskite-type oxides LaFe_{1-x}Co_xO₃ for chemical looping steam methane reforming to syngas and hydrogen co-production. *Applied Energy*, 2016, vol. 168, pp.193 - 203.
- [5] CHISLOVA, I.V. Phase formation processes, structure, and magnetic and catalytic properties of complex gadolinium and strontium ferrites Gd_{2-x}Sr_{1+x}Fe₂O_{7-δ}. *Cand. Sci. (Chem.) Dissertation*, St.Petersburg: St. Peterb. State Univ., 2015. 150 p.
- [6] S. N. RUDDLES DEN AND P. POPPER, New compounds of the K₂NiF₄ type. *Acta Crystallogr.*, 1957, no. 10, pp. 538 - 539.
- [7] BEZNOSIKOV, B.V.; ALEKSANDROV, K.S. Perovskite-like crystals of the Ruddlesden-Popper series., *Crystallography Reports.*, 2000, no 45, pp. 792-798.
- [8] MATHUR B.S. ET AL. Nanocrystalline orthoferrite GdFeO₃ from a Novel Heterobimetallic Precursor. *Adv. Mater.*, 2002, vol. 14, no. 19, pp. 1405 - 1409.