Catalytic performance of LnFeO$_3$ complex oxides for dry reforming of methane to synthesis gas

V. V. Kost[1*], T. A Kryuchkova[1], V. D. Zimina[1], T. F. Sheshko[1],

A. G. Cherednichenko[1], V. V. Kurilkin[2], M. G Safronenko[2], L. V. Yafarova[3]

[1]*Peoples' Friendship University of Russia (RUDN University), Faculty of Science, Physical and Colloidal Chemistry Department, Miklukho-Maklaya str. 6, Moscow, 117198 Russia*
[2]*Peoples' Friendship University of Russia (RUDN University), Faculty of Science, Inorganic Chemistry Department, Miklukho-Maklaya str. 6, Moscow, 117198 Russia*
[3]*Saint-Petersburg State University, Institute of Chemistry, Universitetsky avenue 26, Petergof, St. Petersburg, 198504, Russia*

Nanostructured perovskite-type oxides LnFeO$_3$ (Ln = La, Nd, Gd, Yb, Ho, Lu) were prepared using a method of high-temperature solid state reactions. The effects of lanthanides substitution at the A-site on the catalytic performance of the complex oxides during the dry reforming of methane (DRM) were investigated. It was found that there is a correlation between the nature of the element in A-site of perovskite and its catalytic performances (CH$_4$ and CO$_2$ convention, CO and H$_2$ formation rate). Moreover, the "gadolinium angle" was established in products formation rate, which was related to the features of changing the electronic configuration in lanthanide series.

INTRODUCTION

Currently, due to the growing demand for energy and transportation, excessive amounts of fossil fuels are being used, which leads to negative consequences for the environment. The presence of a large amount of greenhouse gases in the atmosphere is becoming one of the most important socio-environmental issues of the modern world, which requires immediate action [1]. There are several ways to solve this problem; one of them is dry reforming of methane (DRM) to synthesis gas. Methane and carbon dioxide (two main greenhouse gases) are used as reagents, and consequently DRM provides us with an opportunity of their effective disposal. It is also worth noting that the synthesis gas obtained by the DRM process has a CO: H$_2$ ratio close to 1, suitable for further production of valuable liquid fuels by the Fischer-Tropsch method [2-8].

As catalysts for dry reforming of methane, systems of various composition and structure are used. For example, supported catalysts containing transition metals (Ni, Co, Fe) show high activity during the DRM process, but quickly fail by carbon formation on the surface. In fact, the loss of activity *via* carbon deposition does not allow the dry reforming of methane be fully launched on industrial scale. Speaking of precious metal systems, their industrial application is limited because of their high cost. Using the perovskite-type complex oxides as catalysts for DRM allows overcoming these drawbacks due to a well-defined structure, a more dispersed surface and an increased stability [2-8]. Nowadays perovskites have received considerable attention as a serious alternative for various catalytic systems. Their low cost, rather simple synthesis and also the wide range of changing the structure by replacing the elements are responsible for that [9-14]. The experiments [2-8] reveal that the substitution of various metals in the A-position leads to a significant improvement of activity and strongly influences the physicochemical properties of catalysts samples.

EXPERIMENTAL

Preparation

The synthesis of the perovskites LnFeO$_3$ (Ln = La, Nd, Gd, Yb, Ho, Lu) by the method of high-temperature solid state reactions [15] was carried out in an air atmosphere using gadolinium oxide and a transition metal oxide (purity of 99%) as follows:

$$A_2O_3 + Fe_2O_3 = 2AFeO_3 \ (A = La, Nd, Gd, Yb, Ho, Lu)$$
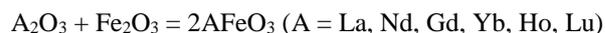
Further the samples were annealed in a muffle furnace at a temperature of 1573 K for 17 hours.

Characterization

The obtained catalysts were evaluated by X-ray diffraction (XRD) using Cu-Kα radiation in an

---

* To whom all correspondence should be sent.
E-mail: kost.veronika6@gmail.com

automated DRON-7 diffractometer (wavelength λ=0.154 nm) with 0.03º (Δ2θ) steps and 3 s counting time in the Bragg angle range of 9º - 80º.

The surface morphology and particle size of the perovskites was investigated by a Zeiss Merlin scanning electron microscope (SEM) with an accelerating voltage of 10 kV, which operates in low vacuum mode and does not require sputtering for non-conducting samples, and with a Carl Zeiss Supra 40VP SEM with a voltage of 20 kV.

The state of iron atoms was determined by Mössbauer spectroscopy on a WISSEL spectrometer. The ^{57}Co isotope in the Rh-matrix with an activity of 10 mKu was used as a source of radioactive radiation; all measurements were carried out at room temperature in the absorption geometry. The α – Fe foil was used to calibrate the velocity scale and the zero position of the chemical shift.

Catalytic tests

The DRM reaction was performed under atmospheric pressure in the temperature range 773-1223 K (flow rates of the reaction mixture - 0.5-1.0 l / h). The catalyst (0.1 g) was loaded into a fixed-bed tubular quartz reactor (1 cm in diameter). The gas mixture was supplied for analysis on a gas chromatograph Crystal 2000M, equipped with thermal conductivity and flame ionization detectors connected in series, in the presence of argon as a carrier gas.

The catalytic properties were evaluated in terms of CH_4 and CO_2 conversions, H_2 and CO selectivity, H_2/CO ratio and carbon deposition, as follows:

$$X(CH_4) = \frac{(nCH_{4_{int}} - nCH_{4_{out}})}{nCH_{4_{int}}} \times 100\% \quad (1)$$

$$X(CO_2) = \frac{(nCO_{2_{int}} - nCO_{2_{out}})}{nCO_{2_{int}}} \times 100\% \quad (2)$$

$$S_{H_2} = \frac{n(H_2)_{form}}{2n(CH_4)_{react}} \times 100\% \quad (3)$$

$$S_{CO} = \frac{n(CO)_{form}}{n(CH_4)_{react} + n(CO_2)_{react}} \times 100\% \quad (4)$$

$$\frac{H_2}{CO} = \frac{n(H_2)}{n(CO)} \quad (5)$$

Carbon balance (%) = $\quad (6)$
$$= \frac{n(CH_4)_{out} + n(CO_2)_{out} + n(CO)_{form}}{n(CH_4)_{int} + n(CO_2)_{int}} \times 100\%$$

RESULTS AND DISCUSSION

Catalyst characterization

The disinct perovskite crystal structure related to single-phase $LnFeO_3$ with an orthorhombic lattice structure was established by X-ray diffraction analysis (Table 1).

The results of scanning electron microscopy revealed that the complex oxides are crystallites of irregular shape with an average particle size of 10 µm. The typical image of SEM observation is shown in Fig. 1 for $GdFeO_3$ as an example.

According to the data of Mössbauer spectroscopy, a single magnetically ordered state of iron is observed in the structure of the perovskite samples - Fe^{3+}.
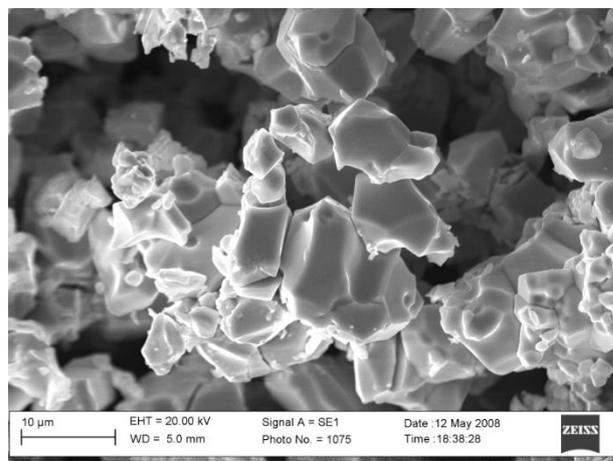

Figure 1. Micrograph of a complex oxide $GdFeO_3$

Table 1. Catalytic characteristics of the studied samples (at T = 1223K).

Sample	Elemental chemical composition		Phase	Iron state
	Ln, mass. %	Fe, mass. %		
$LaFeO_3$	63.80%	36.20%	$LaFeO_3$ perovskite	Fe^{3+}
$NdFeO_3$	66.68%	33.32%	$NdFeO_3$ perovskite	Fe^{3+}
$GdFeO_3$	79.35%	20.65%	$GdFeO_3$ perovskite	Fe^{3+}
$HoFeO_3$	61.84%	38.16%	$HoFeO_3$ perovskite	Fe^{3+}
$YbFeO_3$	66.01%	33.99%	$YbFeO_3$ perovskite	Fe^{3+}
$LuFeO_3$	75.46%	24.54%	$LuFeO_3$ perovskite	Fe^{3+}

Catalytic performance

The perovskite type oxides LnFeO₃ containing different A-site cations (Ln = La, Nd, Gd, Yb, Ho, Lu) were evaluated as catalysts for their performance in dry reforming of methane.

Methane and carbon dioxide conversion

Fig. 2 shows that the reactant conversions did not exceed 10% up to a temperature of 1023 K over LaFeO₃ during the process. A similar pattern was observed in the case of substitution of La by Nd and Gd. Still, further increasing in the reaction temperature led to an improvement in the performance of the catalysts. In high-temperature areas the reactant conversions went up in the following order: LaFeO₃< NdFeO₃ < GdFeO₃. So, at T = 1223 K, methane and carbon dioxide conversion for LaFeO₃ were 20% and 33%, for NdFeO₃ - 21% and 36%, and for GdFeO₃ - 26% and 49%, respectively. According to the obtained values, the introduction of gadolinium in the A-site of the cationic sublattice of the composite oxide caused an increase in the reactant conversions by 5-10% compared with lanthanum ferrite.

Low conversion values were observed over HoFeO₃ and LuFeO₃ perovskite oxides under the DRM whereas the perovskite containing ytterbium as lanthanide in the structure shows superior activity in terms of the conversion of methane and carbon dioxide (34 and 55%, respectively). These results suggest that ytterbium tends to be involved

in side processes (the Boudoir reaction and decomposition of methane), [16] which is indirectly confirmed by the low values of carbon balance (Table 2).

$$2\,CO = C + CO_2 \qquad \Delta H = -172,5 \text{ kJ/mole}$$

$$CH_4 = C + 2\,H_2 \qquad \Delta H = +74,8 \text{ kJ/mole}$$
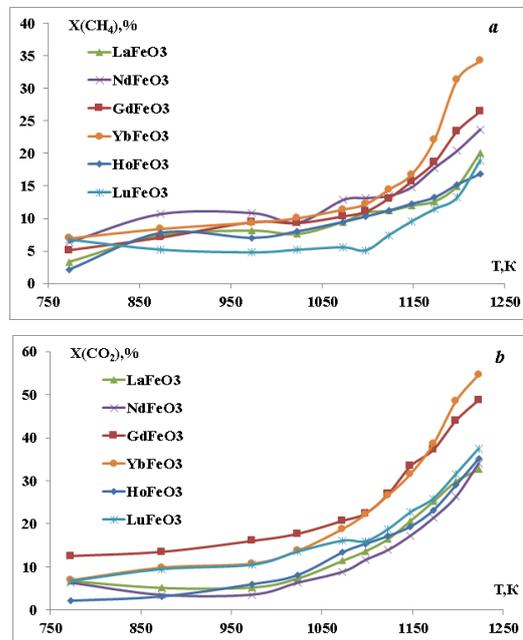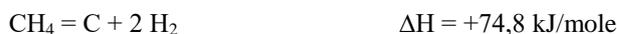
Figure 2. Temperature dependences of CH₄ (a), CO₂ (b) conversions over AFeO₃ (A = La, Nd, Gd, Yb, Ho, Lu)

Table 2. Catalytic characteristics of the studied samples (at T = 1223K)

Sample	X(CH₄), %	X(CO₂), %	r (CO), mole/(h*g)	r (H₂), mole/(h*g)	S(CO), %	S(H₂), %	H₂/CO	Carbon balance, %	Electronic configuration
LaFeO₃	20	33	0.096	0.025	87	29	0.26	96	$4f^0\,5d^1\,6s^2$
NdFeO₃	21	36	0.106	0.038	74	36	0.36	92	$4f^4\,6s^2$
GdFeO₃	26	49	0.130	0.046	76	38	0.36	91	$4f^7\,5d^1\,6s^2$
HoFeO₃	17	35	0.096	0.029	85	39	0.30	96	$4f^{11}\,6s^2$
YbFeO₃	34	55	0.088	0.030	58	25	0.34	81	$4f^{14}\,6s^2$
LuFeO₃	19	38	0.094	0.031	79	39	0.33	94	$4f^{14}\,5d^1\,6s^2$
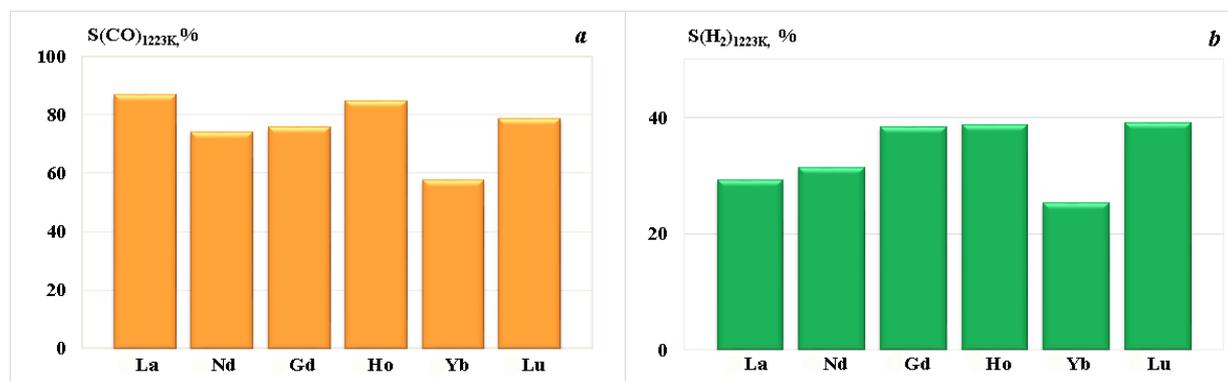
Figure 3. CO (a) and H₂ (b) selectivities for the perovskite oxides in the high-temperature area

Selectivity and H₂/CO ratio

Fig. 3 represents the temperature dependences of the carbon monoxide and hydrogen selectivities. It follows that an increase in temperature leads to the growth of CO and H_2 selectivities for all the studied samples. $AFeO_3$ (A = Gd, Ho, Lu) are worth noting since carrying out the reaction on these perovskites allows to obtain a higher value of hydrogen selectivity (40%). However, with respect to CO, such dependence was not observed: carbon monoxide S (CO) reached a maximum over $LaFeO_3$ perovskite compared with the other samples.

Fig. 4 presents the temperature dependence of the syngas ratio for all catalyst samples. The diagram clearly demonstrates the maximum value of 0.36 observed over $GdFeO_3$ and $NdFeO_3$ oxides.
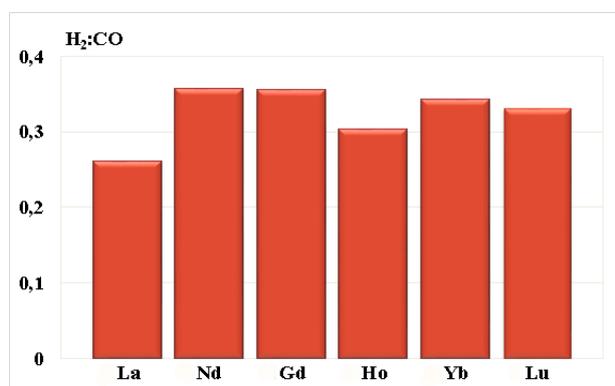

**Figure 4**. H₂:CO ratio for all catalyst samples in the high-temperature area
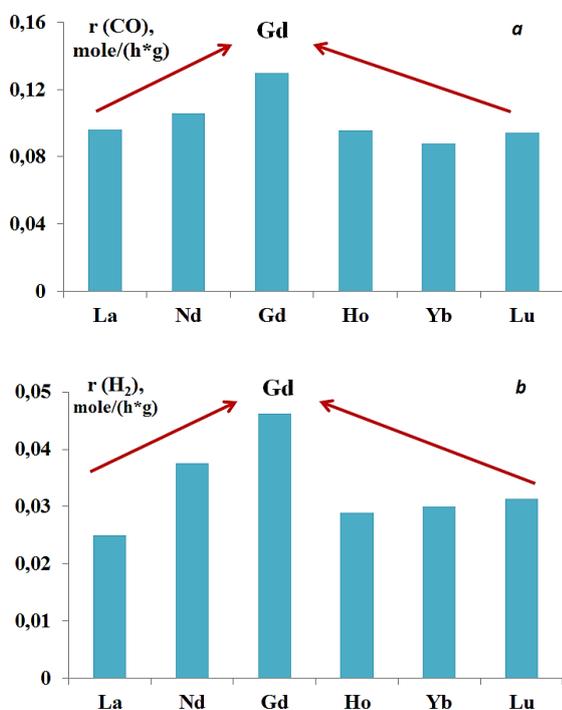
Figure 5. The formation rate of CO (a) and H₂ (b) depending on the nature of the element in the A-position

Formation rate of syngas and the gadolinium angle

Analysis of the obtained experimental data revealed some dependence on the nature of the A-element for all studied catalysts: the rates of hydrogen and carbon monoxide formation reached a maximum on $GdFeO_3$ (Fig. 5) that is the so-called "gadolinium angle" [17, 18].

Most likely, the appearance of the "gadolinium angle" in the catalytic properties is associated with the peculiarities of the electronic configuration change in the lanthanide series. Starting with lanthanum and moving towards gadolinium the number of electrons at the 4f-level increases, while the 5d-level remains unoccupied. An additional electron occupies the 5d level in gadolinium structure, forming the $4f^7 5d^{16} s^2$ electron configuration. The next element in the lanthanide series (terbium) is characterized by transition of the 5d-electron to the 4f- level ($4f^9 6s^2$) as well as cerium. Further, up to ytterbium, a monotonous increase in the number of electrons to $4f^{14}$ is observed [17]. Moreover, gadolinium has the largest ion radius among others in the Ln^{3+} series [18]. Thus, it can be assumed that the Me-CO_2 bond weakens on moving from La and Lu to Gd, which promotes the dissociative adsorption of carbon dioxide and increases the rate of CO formation.

CONCLUSIONS

In this study, the catalytic activity of complex perovskite-type oxides $AFeO_3$ (A = La, Nd, Gd, Ho, Yb, Lu) was investigated in dry reforming of methane. It was considered that methane conversion does not depend on the nature of the element in the A-position of the catalyst structure. Furthermore, a correlation between the nature of the element in the cation sublattice (A-position) and the catalytic characteristics of perovskite (CO_2 conversion and the rate of CO formation) was established. Our results also suggest the presence of a "gadolinium angle" in the rate values of products formation, which is connected with the peculiarities of electronic configuration changes in the lanthanide series.

REFERENCES

1. O. Edenhofer, R. Pichs-Madruga, Y. Sokona, E. Farahani, S. Kadner, K. Seyboth, et al. Climate change 2014: mitigation of climate change – contribution of Working Group III to the fifth assessment report of the Intergovernmental Panel on Climate Change, Cambridge, Cambridge University Press, 2014, p. 603.

2. K. Sutthiumporn, T. Maneerung, Y. Kathiraser, S. Kawi, CO$_2$ dry-reforming of methane over La$_{0.8}$Sr$_{0.2}$Ni$_{0.8}$M$_{0.2}$O$_3$ perovskite (M = Bi, Co, Cr, Cu, Fe): Roles of lattice oxygen on C–H activation and carbon suppression, Department of Chemical & Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 119260, Singapore

3. X. Gao, Zh. Tan, K. Hidajat, S. Kawi, *Catalysis Today,* **281**, 250 (2017).

4. J. Juan-Juan, M. C. Roman-Martinez, M. J. Illan-Gomes, *Applied Catalysis A: General,* **355**, 27 (2009).

5. M. Radlik, M. Adamowska-Teyssier, A. Krzton, K. Kozieł, W. Krajewski, W. Turek, P. da Costa, *C. R. Chimie*, **18**, 1242 (2015).

6. B. de Caprariis, P. De Filippis, V. Palma, A. Petrullo, A. Ricca, C. Ruocco, M. Scarsella, *Applied Catalysis A: General,* **517**, 47 (2016).

7. A. Erdohelyi, K. Fodor, F. Solymosi Proc. IV Int. National Gas Conversion Symp. Kruger National Park, South Africa, 1995. Amsterdam, Elsevier, 1997, p. 525.

8. J. H. Bitter, V. Seshan, J. A. Lercher, *J. Catal.*, **171**, 279 (1997).

9. W. F. Libby, *Science,* **171**, 499 (1971).

10. R. J. H. Voorhoeve, J. P. Remeika, P. E. Freeland, B. T. Matthias, *Science*, **177**, 353 (1972).

11. R. J. H. Voorhoeve, J. P. Remeika, D. W. Johnson, *Science*, **180**, 62 (1973).

12. P. K. Gallagher, D. W. Johnson Jr., F. Schrey, *Mater. Res. Bull.,* **9**, 1345 (1974).

13. V. M. Gonzalez-Delacruz, F. Ternero, R. Pereniguez, A. Caballero, J.P. Holgado, *Appl. Catal. A: Gen.,* **384**, 1 (2010).

14. T. Odedairo, J. Chen, Z. Zhu, *Catal. Commun.*, **31**, 25 (2013).

15. J. Gregory, McCarthy, V. Paul, The Pennsylvania State University, Crystal chemistry of catalyst materials. I. Composition and unit cell parameters of «ReMnO$_3$» Phases prepared in air, p. 1277.

16. K. Świrk, M. E. Gálvez, M. Motak, T. Grzybek, M. Rønning, Patrick Da Costa, *Journal of CO$_2$ Utilization,* **27**, 247 (2018).

17. G. V. Ionova, V. G. Vokhmin, V. I. Spitsyn, Regularities of the change in the properties of lanthanides and actinides, Moscow, Nauka, 1990, p. 7.

18. G. A. Bandurkin, B. F. Dzhurinsky, I. V. Tananaev, Crystal chemistry features of compounds containing rare-earth metals, Moscow, Nauka (Chemistry of Rare Elements), 1984, p.190, 203.