EFFECT OF THE B-SITE CATION IN $GdBO_3$ (B = Fe, Mn, Co) PEROVSKITE-TYPE OXIDES ON CATALYTIC PERFORMANCES FOR SYNGAS PRODUCTION

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Abstract

Perovskite-type compounds are an important class of materials and there are extensively studied in high-temperature catalytic processes. Dry (carbon dioxide) reforming of methane (DRM) to synthesis gas is one of the most important reactions using such materials as catalysts. In this study, perovskite-type complex oxides $GdBO_3$ (B = Fe, Mn, Co) applied as catalysts for syngas production via dry reforming of methane. These samples were obtained by ceramic technology and were investigated by means of X-ray diffraction, scanning electron microscopy, Mossbauer microscopy, and X-ray photoelectron spectroscopy. Catalytic activities were evaluated at atmospheric pressure in the temperature raised from 773 to 1223 K under continuous flow of reactant gases with a CH_4:CO_2 = 1:1 ratio. The test samples catalytic activity depends on the oxygen stoichiometry in the complex oxide. Thus, the presence of oxygen vacancies in the perovskite containing cobalt cation in the B-site of the perovskite structure proved to be favorable for DRM. It was on this sample that conversions of CH_4 and CO_2 were the maximum values of 99 and 97% at 1223 K, respectively, while syngas was obtained with H_2/CO molar ratio close to unity. Besides, $GdCoO_3$ showed the high stability in the DRM process: the catalytic performances retained more than 110 h time. The presence of oxygen vacancies is probably due to the crystallographic radius size of the cation introduced into the B-site of the complex oxide. Therefore, the catalytic activities of the investigated samples increased in the order: $GdMnO_3$ < $GdFeO_3$ < $GdCoO_3$.

Keywords: Perovskite-type oxide, syngas, dry reforming of methane, activity, oxygen mobility

1. INTRODUCTON

In recent years, great attention has been paid to alternative methods for syngas production, in particular carbon dioxide conversion of hydrocarbons, such as methane (the so-called dry (carbon dioxide) reforming of methane (DRM)) [1]. Moreover, this type of methane conversion is characterized by a reduction in energy consumption compared to current methane reforming processes: steam reforming, partial oxidation and autothermal reforming [2].

However, the main impediment to using DRM in industry is that at present there are practically no catalysts that would not be deactivation as a result of coke formation.

And today the perovskites as a serious alternative to platinum group metals (PGMs) are regarded as catalysts for various catalytic processes, including the DRM process, mainly due to the simplicity of their synthesis and low cost compared to the PGMs, and also because of a wide range of changes in their structure by substitution of elements, which makes it possible to synthesize a selective catalyst for a narrower field of its application [3-7].

Plural studies [8-12] of the perovskites catalytic activity have shown their high stability and activity for syngas production by the DRM method, which makes these systems promising for further study.

The aim of the present work was to investigate the use of perovskite-type oxides $GdBO_3$ (B = Fe, Mn, Co) as catalysts for syngas production during the dry reforming of methane under continuous flow of reactive gases.

2. EXPERIMENTAL PART

2.1. Catalyst preparation

Perovskite-type ferrites, $GdBO_3$ (B = Fe, Mn, Co) were investigated as catalysts for dry reforming of methane. These samples were prepared by ceramic technology in air from oxides of gadolinium and transition metal (99% purity) followed by cooling in the furnace:

$$Gd_2O_3 + B_xO_y = GdBO_{3\pm\delta} \quad (B = Fe, Mn, Co)$$

Heat treatment of the sample was as follows:

Calcination:

- $GdFeO_3$ - 1573 K for 17h;
- $GdMnO_3$ - 1473 k for 30h;
- $GdCoO_3$ - 1373 K for 40h.

2.2. Catalyst characterization

Several techniques such as X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Mossbauer microscopy, and X-ray photoelectron spectroscopy (XPS) were employed for characterization of the investigated samples.

XRD was performed on a Thermo ARL X'TRA diffractometer using CuK_α radiation. The SEM images of synthesized samples were obtained on Carl Zeiss EVO 40EP and Zeiss Supra 40VP scanning electron microscopes. Mössbauer spectra have been recorded at room temperature by using spectrometer Wissel (^{57}Co in a rhodium matrix with activity 10 mKu), the isomeric shifts were calculated with respect to α-Fe. In order to evaluate the part of paramagnetic species the intensity of the signals was determined precisely up to the factor of resonance absorption.

2.3. Catalyst evaluation

The catalyst performance in dry reforming of methane was evaluated in a quartz tubular microreactor, containing 0.1 g of the sample dilute in 0.5 g of quartz to increase the surface area. The activity test was carried out at the temperature range 773-1223 K, under atmospheric pressure with a feed composition of $CH_4:CO_2$ = 1:1 and a total flow of 0.9 - 1 l/h. The gaseous effluent was analyzed on line using a gas chromatograph instrument (Crystal 2000M; a column of stainless steel filled with Porapack Q at 393K, argon as a carrier gas) equipped with a thermal conductivity and flame ionization detectors for detecting CO_2, CH_4, H_2 and CO.

The CH_4 and CO_2 conversions (α_i) were calculated using equation 1 and are defined as the CH_4 and CO_2 converted per total amount of CH_4 and CO_2 fed, respectively:

$$\boldsymbol{\alpha_i}\,(\%) = \frac{\boldsymbol{n_{int}} - \boldsymbol{n_{out}}}{\boldsymbol{n_{int}}} \quad (\mathbf{1})$$

The selectivity (S) to CO was calculated based on carbon balance and defined as:

$$\boldsymbol{S_{CO}}(\%) = \frac{\boldsymbol{n(CO)}}{\boldsymbol{n(CH_4)_c} + \boldsymbol{n(CO_2)_c}} \times \mathbf{100} \quad (\mathbf{2})$$

While hydrogen selectivity was calculated as:

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

And H_2/CO ratio was calculated as:

$$\frac{H_2}{CO}\ ratio = \frac{n(H_2)}{n(CO)} \quad (4),$$

where n(CO) and $n(H_2)$ are the moles of carbon monoxide and hydrogen produced and $n(CH_4)_c$ and $n(CO_2)_c$ are the amounts of methane and carbon dioxide converted, as previously reported in literature [13-14].

3. RESULTS AND ITS DISCUSSION

The obtained samples of complex oxides refer to the Ruddlesden-Popper phases and have a perovskite-type structure of the ABO_3 type. According to XRD data, all initial samples are single-phase. **Figure 1** shows the XRD spectra of $GdFeO_3$ complex oxide as an example.

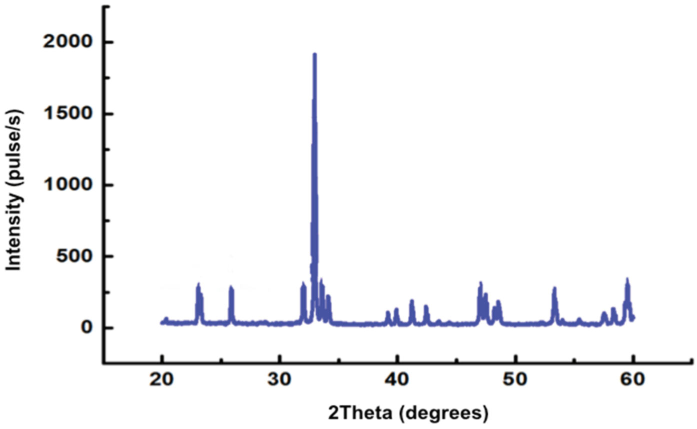

Figure 1 XRD pattern of the $GdFeO_3$ complex oxide

The scanning electron microscopy (SEM) data (**Figure 2**) shows that the ceramic technology makes it possible to obtain particles of complex oxides about 200 nm in size.

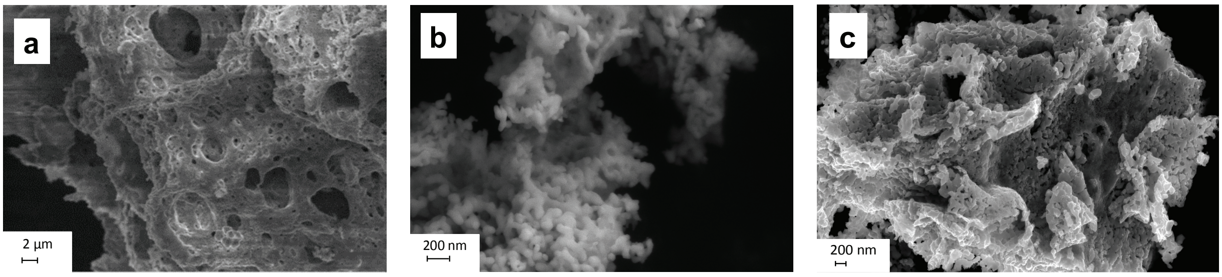

Figure 2 SEM images of perovskite catalysts: a - $GdFeO_3$; b - $GdMnO_3$ and c - $GdCoO_3$

The Mössbauer spectra of $GdFeO_3$ showed that the iron atoms in the ferrite are in a single state - Fe^{3+}. The state of Co and Mn atoms in perovskites was investigated by the XPS method and the presence of atoms was revealed Co and Mn in two states: Co^{2+}, Co^{3+} and Mn^{2+}, Mn^{4+}, respectively.

The reaction of CH_4 and CO_2 was studied at the temperature range 773-1223 K under atmospheric pressure. The experimental results are regrouped in **Figure 3**. It was shown that no appreciable conversions of the reagents were observed before T = 1023 K; CH_4 and CO_2 conversions over all investigated samples barely reached 15%. But a further rise in temperature led to an increase in the process rate. Also it was found that the CO_2 conversion was higher than that of methane in all cases except $GdCoO_3$ (**Figure 3**). Only CO, H_2 and a small amount of water were detected.

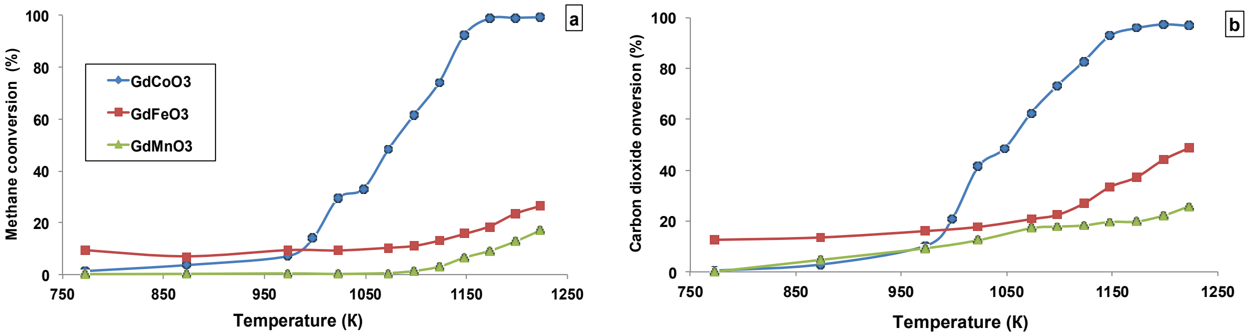

Figure 3 The (a) methane and (b) carbon dioxide conversion over $GdBO_3$ (B = Fe, Mn, Co) complex oxides

Table 1 summarizes the catalytic parameters obtained in the methane dry reforming at 1273 K over $GdBO_3$ (B = Fe, Mn, Co) complex oxides. Comparing the CH_4 and CO_2 conversions obtained on different catalysts, we can conclude that the activity was the highest on the $GdCoO_3$ sample. Thus, at T = 1223 K, the methane and carbon dioxide conversion were 99% and 97%, respectively, compared to ferrite and manganite (**Figure 3, Table 1**), where the CH_4 and CO_2 conversion values barely reached 30% and 50%, respectively. Hydrogen selectivity was 79%, and the synthesis gas ratio was close to the stoichiometric ratio for Co-containing sample.

Table 1 The catalytic performances of $GdBO_3$ perovskite-type oxides for dry reforming of methane

Catalyst	**B - ion**	**$r_{3^{3+}}$, nm**	**T =1223 K**				
			α (CH_4), %	**α (CO_2), %**	**S(CO), %**	**S(H_2), %**	**H_2:CO**
$GdCoO_{3-\delta}$	Co^{3+}	0.064	99	97	74	79	1.06
$GdFeO_3$	Fe^{3+}	0.067	26	49	76	38	0.36
$GdMnO_{3+\delta}$	Mn^{3+}	0.072	17	26	68	15	0.17

Perhaps the differences in catalytic activity are associated with the so-called oxygen mobility in the perovskite structure: it is suggested that the oxygen non-stoichiometry depends on the crystallographic radius size of the metal ion introduced into the B-site of the complex oxides, which is confirmed by the literature [15-17]. And the presence of oxygen vacancies in $GdCoO_{3-\delta}$ turned out to be favorable for the synthesis gas production by dry reforming of methane.

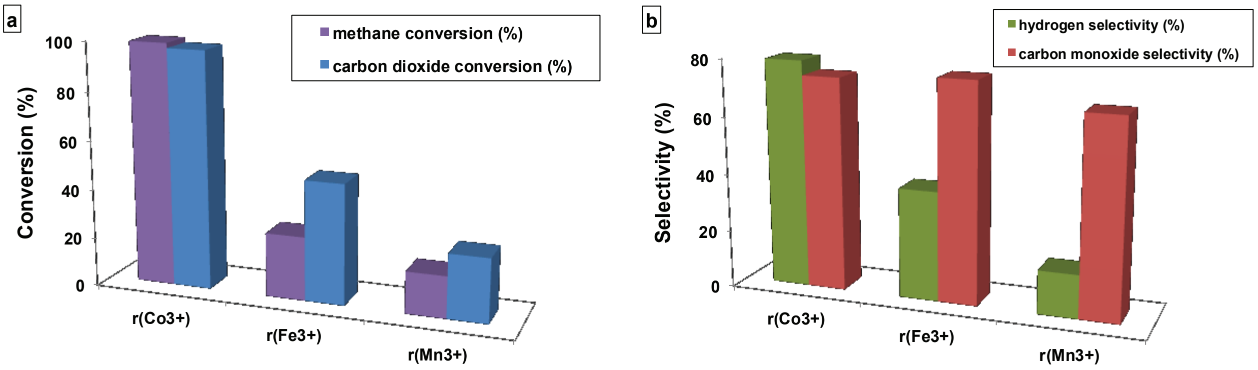

Figure 4 The (a) conversion and (b) selectivity dependences on the B-ion radius of complex oxides

On the basis of the data obtained revealed an inverse relationship between the catalytic activity of investigated samples and the crystallographic radius of the B-site ion, as illustrated the diagram on **Figure 4**, and the catalytic activity increased in the following order: $GdMnO_3 < GdFeO_3 < GdCoO_3$.

However, it should be noted that in the case of CO selectivity, a small maximum for ferrite is observed (**Figure 4b**). Perhaps the increase of S(CO) over the ferrite is due to the fact that the process of reverse water-gas shift reaction, which complicated the carbon dioxide reforming of methane, is better on systems containing iron in its composition [18-19].

The study of the catalyst productivity with the highest activity ($GdCoO_3$) in the periodic mode (repeat heating and cooling modes) at T = 1173 K demonstrated its high stability: the catalytic characteristics remained unchanged for more than 110 operating hours (**Figure 5**).

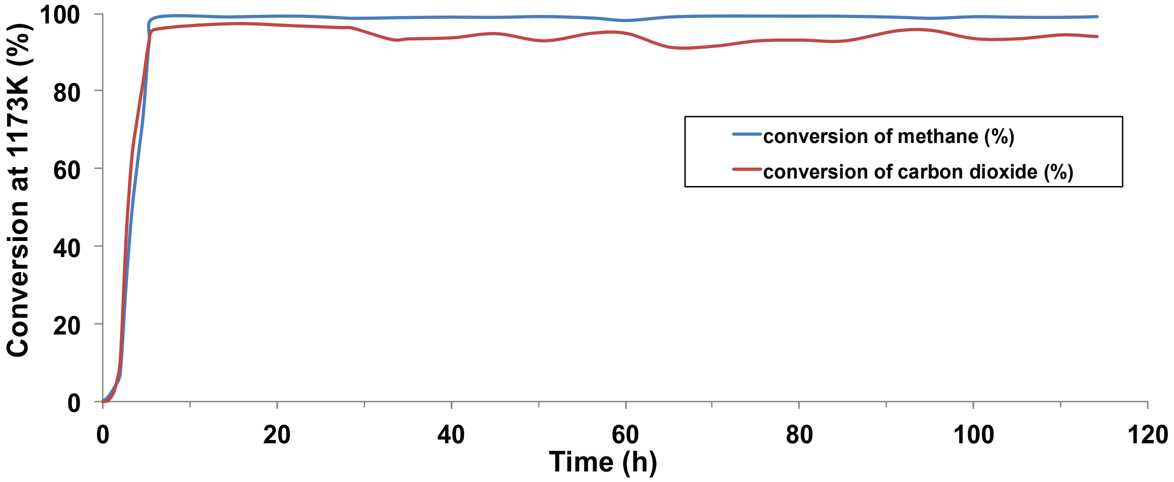

Figure 5 The time dependence of CH_4 and CO_2 conversion of $GdCoO_3$ complex oxide

4. CONCLUSION

The influence of the B-site cation in complex oxides on their catalytic activity for syngas production via dry reforming of methane was studied. It was noted that the catalytic activity of the test samples depends on the oxygen stoichiometry in the perovskite structure. Thus, the oxygen vacancies presence in perovskite containing cobalt in the B-site of perovskite structure proved to be favorable for obtaining synthesis gas by the DRM. It was also noted that the oxygen vacancies presence is probably due to the crystallographic radius size of the cation introduced into the B-site of the complex oxide.

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