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Synthesis, characterization, and catalytic properties of GdCoO_3 for dry reforming of methane

REGINA K. ALLABERGENOVA^{1*}, DARIA A. BOBKOVA¹, ELIZAVETA M. BORODINA¹, TATIANA A. KRYUCHKOVA^{1,2*}, EKATERINA B. MARKOVA¹, TATIANA F. SHESHKO¹, NIKOLAI N. LOBANOV³ and ALEXANDER G. CHEREDNICHENKO¹

¹Physical and Colloidal Chemistry Department, Faculty of Science, RUDN University, 6 Miklukho-Maklaya St, Moscow, 117198, Russian Federation, ²Moscow Pedagogical State University, MPGU, 1/1 Malaya Pirogovskaya Str., Moscow, 119991, Russian Federation and ³Inorganic Chemistry Department, Faculty of Science, RUDN University, 6 Miklukho-Maklaya St, Moscow, 117198, Russian Federation

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Abstract: Perovskite oxides (ABO_3) due to their high thermal stability and the ability to control the physico-chemical properties are considered as an alternative to traditional catalysts containing noble and transition metals. Herein, the recent research breakthroughs of GdCoO_3 catalysts in experimental studies are summarized in detail. First, the perovskite-type GdCoO_3 complex oxides were obtained by co-precipitation method with the various precipitators and were characterized by X-ray diffraction (XRD), low temperature nitrogen adsorption and IR spectroscopy. Physical and chemical analysis showed that the choice of precipitant doesn't significantly affect the phase composition of the perovskites. The catalytic performance of gadolinium cobaltites was discussed. It was found that the use of cobaltites obtained by co-precipitation leads to the inhibition of the side reaction of the reverse steam reforming of carbon monoxide. Finally, the investigation of the used catalysts demonstrated the formation of $\text{Gd}_2\text{O}_2\text{CO}_3$ and metallic cobalt, which indicates the nature of active centres: gadolinium is the centre of CO adsorption, while hydrogen chemisorption occurs on cobalt-sites.

Keywords: synthesis gas; catalysis; perovskites; cobalt; conversion.

INTRODUCTION

As of this date, oil remains the main source of raw materials to produce motor fuel and products of the main organic synthesis. Demand for oil largely depends on the current economic situation and prices for oil products. However,

* Corresponding author. E-mail: r.allabergenova.25@gmail.com, kryuchkova-ta@rudn.ru
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the volume of natural oil production is growing every year, and these volumes barely have time to cover the existing needs. According to the forecasts of the International Energy Agency, the onset of “peak oil” (maximum world oil production) should be expected in 2030, after which there will be a decline in production volumes around the world. For this reason, today much attention is paid to the development of GTL (gas-to-liquids) technology. GTL is the production of petroleum products from natural gas or associated petroleum gas, about 30 % of which in Russia is simply burned by flares after production. At the same time, efforts worldwide to reduce CO₂ emissions are driving growing research interest in finding effective ways to chemically activate this inert molecule. Catalytic processes are of utmost importance in this area, while renewable energy sources are the most suitable to provide these high-energy transformations.¹

In this context, carbon dioxide conversion of methane (dry reforming of methane, DRM), as the first stage of GTL technology, is an attractive way for the transition from the use of fossil resources to the effective conversion of CO₂ and CH₄ into synthetic fuel, because the resulting synthesis gas can subsequently be converted by the Fischer-Tropsch synthesis into various hydrocarbon fractions.¹

Moreover, the reaction is environmentally beneficial, because two greenhouse gases are used in it:²



DRM is an endothermic process, and it is carried out at operating temperatures above 1000 K, and this requires heat-resistant catalysts with high productivity. Most often, supported catalysts based on noble metals such as Rh, Ru or Ir are used for this process.³ Transition metals such as Ni, Co, Fe can also be effectively used as an alternative and cost-effective active phase.³

In most cases, the most common metallic, bimetallic and oxide catalysts have low selectivity and are rapidly deactivated by sintering and carburizing the surface, which reduces their efficiency in the DRM. Therefore, the search for the most suitable catalyst for this process is an urgent task for many scientists. In this regard, the properties of complex oxides with the structure of perovskite are being studied. These compounds are stable at high temperatures, easy to prepare and have a lower cost than noble metal catalysts. Another interesting feature of perovskites is the ability to regulate catalytic characteristics by varying their chemical composition at the A- and B-positions.⁴⁻⁸ For example, in previous work⁹ on the study of LnFeO₃ under DRM conditions, it was shown that the maximum catalytic activity was observed on samples containing gadolinium in the A-position, which contributed to the further study of gadolinium-containing complex oxides. And the study of GdMeO₃ (Me = Fe, Co, Mn) obtained by solid phase¹⁰ synthesis revealed the influence of the nature of the B-element on the efficiency of the catalyst. Moreover, in addition to varying the chemical compo-

sition, the characteristics of active centres of systems can be influenced by the synthesis method,¹¹ which leads to a change in its catalytic properties, and this has also been confirmed in our previous works.^{9,10}

The purpose of this work was to study the catalytic properties of complex oxides with the perovskite structure of the GdCoO₃ composition under conditions of carbon dioxide conversion of methane, as well as to identify the correlation “synthesis conditions – physicochemical properties – catalytic characteristics”.

EXPERIMENTAL

The synthesis of complex oxides GdCoO₃ was carried out by the co-precipitation method using solutions of sodium hydroxide and ammonium carbonate as precipitators.^{12,13} The synthesized GdCoO₃ oxides are respectively named as GCO_{precipitator}.

GCO_{NaOH}. For the synthesis of GCO_{NaOH} 3 mol Gd(NO₃)₃·6H₂O and 4 mol Co(NO₃)₂·6H₂O were dissolved in 40 mL of water. 0.027 mol of anhydrous glucose, 0.08 mol ethylene glycol and 60 mL of 4M NaOH solution was added to the resulting solution. The pH of the solution was adjusted to 10 by dropwise addition of 15 mL of 5.4 M HNO₃. A suspension was obtained and held for 24 h in a drying oven at 100 °C. The brown precipitate was filtered and washed with more water, then annealed in a muffle oven for 3 h at 300 °C and 4 h at 700 °C.

GCO_{(NH₄)₂CO₃}. For the synthesis of GCO_{(NH₄)₂CO₃} stoichiometric proportions of Gd(NO₃)₃·6H₂O and Co(NO₃)₂·6H₂O were dissolved in a small amount of distilled water and stirred for 2 h at 80 °C. Next, the calculated amount of (NH₄)₂CO₃ was also dissolved in distilled water and then slowly added to the first solution. The resulting suspension was stirred for 3 h at 80 °C. The precipitate was filtered on a Buchner funnel and washed with distilled water to give a colourless filtrate. The precipitate was then transferred to porcelain crucibles, dried for 12 h at 120 °C, and calcined for 10 h at 850 °C.

Physical and chemical methods of catalysts research

X-ray phase analysis was carried out on the device Rigaku MiniFlex II X-ray diffractometer with Cu anode (K α radiation = 1.5418 Å).

IR spectra of the samples were obtained on a Nicolet 6700 spectrophotometer. The samples were prepared in powder form for all catalysts. Sample preparation was performed by impaired total internal reflection (ATR). Equipped with polycrystalline diamond prefix was used. Spectra were obtained in the mid and far IR regions (4000–400 cm⁻¹).

The parameters of the porous structure of the samples were determined from isotherms of nitrogen vapour adsorption at 77 K temperature measured at the ASAP 2020-MR Micromeritics automatic high-vacuum unit (USA) in the range of relative vapour pressures from 0.001 to 0.98. Previously, the samples were evacuated to a residual vacuum of less than 10⁻⁷ mm Hg without heating.

Catalytic tests

The reaction of dry reforming of methane over synthesized catalysts was carried out in a flow-through mode in the temperature range of 773–1223 K at atmospheric pressure and the reaction mixture flow of 0.9–1.0 L/h. The ratio of the reactants was CO₂:CH₄ 1:1, the catalyst weight in all experiments was 0.1 g. The catalyst was mixed with quartz in a ratio of 1:1 in order to avoid the formation of hot spots in the catalytic bed alongside with increasing the

volume. Analysis of the composition of the reaction mixture was carried out on a Crystal 2000 M chromatograph (carrier gas – argon, column length – 2 m, diameter – 3 mm, sorbent – Porapak Q) using a flame ionization detector and a heat conductivity detector connected in a series. Catalytic characteristics such as methane and carbon dioxide (X) conversions, selectivity (S) of reaction products were determined and calculated.

Conversion of CH_4 and CO_2 reactants were calculated using the formula:

$$X_i = 100(n_0 - n) / n_0 \quad (2)$$

where n – the amount of CH_4 or CO_2 in exhaust gas, mol; n_0 – initial amount of product in the reaction mixture, mol.

Hydrogen selectivity was calculated as the ratio of hydrogen generated to the total amount of methane reacted:

$$S_{\text{H}_2} = 100n(\text{H}_2) / 2n(\text{CH}_4)_{\text{reacted}} \quad (3)$$

Carbon monoxide selectivity was calculated as the ratio of CO generated to total CH_4 and CO_2 , reacted:

$$S_{\text{CO}} = 100n(\text{CO}) / (n(\text{CH}_4)_{\text{reacted}} + n(\text{CO}_2)_{\text{reacted}}) \quad (4)$$

Carbon balance was calculated as:

$$\text{Carbon balance} = 100 \frac{n_{\text{ur}}(\text{CH}_4) + n_{\text{ur}}(\text{CO}_2) + n(\text{CO})}{n_0(\text{CH}_4) + n_0(\text{CO}_2)} \quad (5)$$

where $n_{\text{ur}}(\text{CH}_4)$ and $n_{\text{ur}}(\text{CO}_2)$ – unreacted amount of CH_4 and CO_2 , mol; $n_0(\text{CH}_4)$ and $n_0(\text{CO}_2)$ – initial amount of CH_4 and CO_2 , mol; $n(\text{CO})$ – amount of CO in reaction mixture, mol.

The quantification error of each component included a measurement error of the temperature and feed rate of the reaction mixture and did not exceed 5 %.

RESULTS AND DISCUSSION

The reaction of DRM over GCO oxides obtained by co-precipitation method showed their high catalytic activity in comparison with the previously studied oxides.^{9,10} At temperatures above 950 K, there was a sharp rise in CH_4 and CO_2 conversions to 80–90 %. Almost complete transformations of the reactants were achieved at 1100 K and these indicators did not decrease with a further rise in temperature (Fig. 1). It is worth noting that on the sample obtained with NaOH as the precipitant, significant CH_4 conversions were observed about 50 K lower than on the sample obtained with $(\text{NH}_4)_2\text{CO}_3$. Moreover, the choice of precipitator was somewhat affected by the selectivity of the reaction products when the highest values were achieved on the sample obtained in the presence of ammonium carbonate as the precipitator (Table I).

It was found that the hydrogen selectivity values on the test samples were significantly higher than the carbon monoxide selectivity values, which in turn leads to high ratio values $\text{H}_2:\text{CO}$ of 1.5–2. High “non-stoichiometric” values of the synthesis gas ratio for the classical process may indicate the possibility of side reactions involving methane. Indeed, in parallel with the decrease in carbon monoxide selectivity, a sharp increase in the degree of carbonization of the cat-

alysts surface was observed in the temperature range 1073–1223 K. The carbon balance value did not exceed 65 %.

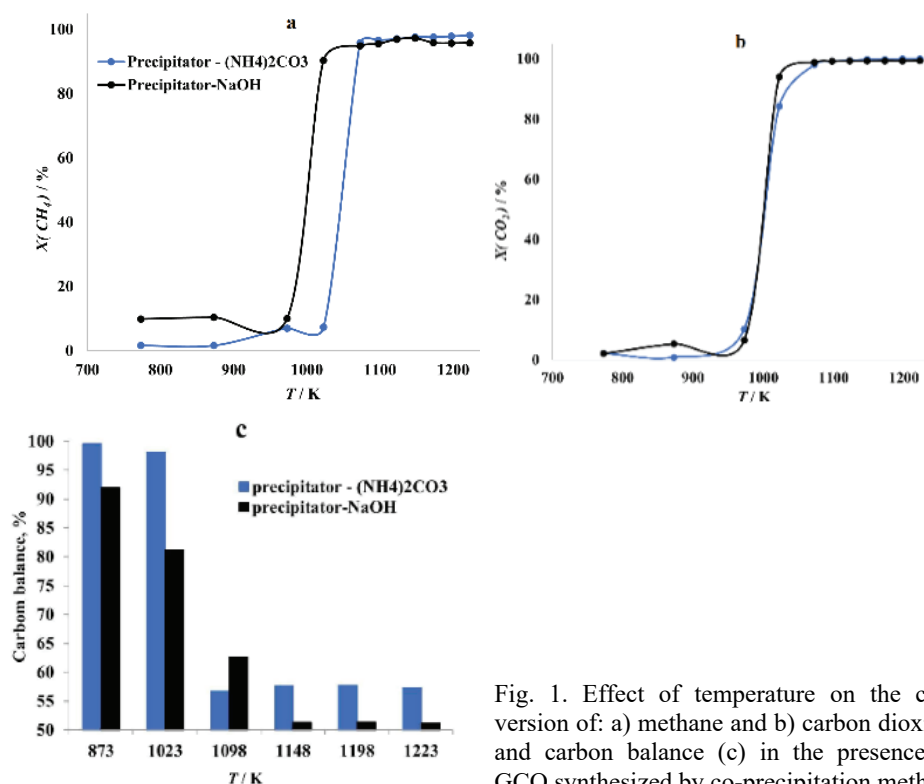
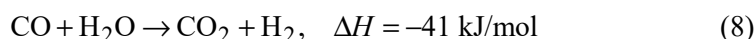
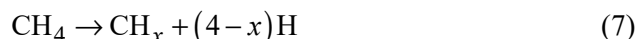
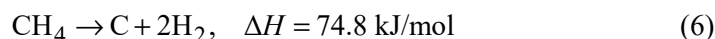


Fig. 1. Effect of temperature on the conversion of: a) methane and b) carbon dioxide, and carbon balance (c) in the presence of GCO synthesized by co-precipitation method.

TABLE I. Catalytic performance of GCO catalysts in the temperature range 1123–1223 K

Parameter	GCO _{(NH₄)₂CO₃}			GCO _{NaOH}		
	<i>T</i> / K					
	1123	1173	1223	1123	1173	1223
$S(\text{H}_2) / \%$	99	99	99	89	81	76
$S(\text{CO}) / \%$	57	56	56	48	45	57
$n(\text{H}_2)/n(\text{CO})$	1.82	1.90	1.99	1.96	1.90	1.41
$X(\text{CH}_4)/X(\text{CO}_2)$	0.98	0.98	0.98	0.98	0.97	0.96

According to the literature data,¹⁴ the increase in hydrogen selectivity, the ratio of synthesis gas components and a noticeable decrease in carbon balance indicate the occurrence of various side processes along with the DRM reaction, among which the methane decomposition reaction carried out in two directions (Eqs. (6) and (8)), as well as the reverse steam conversion of CO (Eq. (8)) prevail under these conditions:



Confirmation of the reaction (8) can be the formation of water in the reaction products, as well as the ratio $X(\text{CH}_4)/X(\text{CO}_2) < 1$.¹⁵ Analysis of the obtained results and comparison with previously studied systems^{9,10} suggests that the use of GCO obtained by co-precipitation method as a catalyst leads to suppression of the reverse steam conversion reaction of CO. Indeed, we see that the ratio $X(\text{CH}_4)/X(\text{CO}_2) \approx 1$ and water in reaction products for the considered interval of temperatures is registered only in insignificant quantity. At the same time, the formation of carbon deposits on the catalyst surface and the practical absence of hydrocarbons in the products indicate a more intensive side reaction of decomposition (Eq. (7)). Samples of GCO oxides were characterized by a set of methods of physicochemical analysis. Fig. 2 demonstrates results of X-ray phase analysis of the GCO complex oxide before (a) and after (b) catalysis. Sample diffractograms turned out to be similar to those described in the literature for gadolinium cobaltites.¹⁶

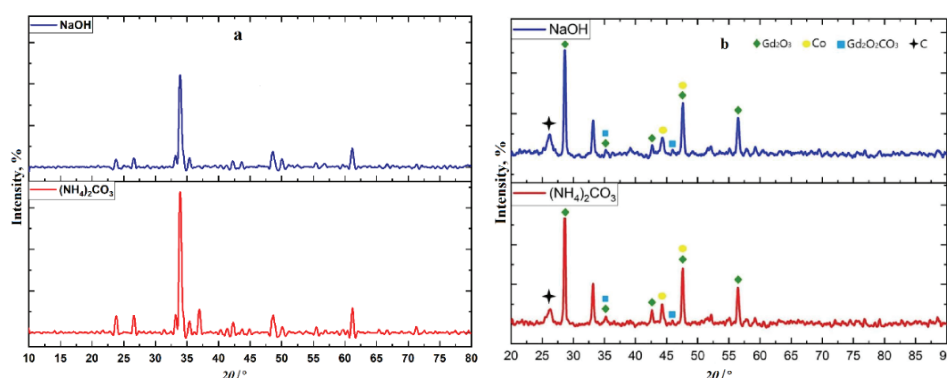


Fig. 2. XRD patterns of the GCO complex oxide before (a) and after (b) catalysis.

Testing the catalysts stability was carried out in a periodic mode (heating the catalyst to the experimental temperature ($T = 1173 \text{ K}$), keeping it in isothermal conditions for 9–10 h, cooling in the reaction medium to room temperature and repeating all stages of the experiment, number of cycles – 3). Table II demonstrates results of the catalytic experiment. It was shown that the samples, regardless of the preparation method and high surface carbonization, do not lose their activity in the DRM reaction: the catalytic characteristics remained practically unchanged for more than 30 h of operation under reaction conditions (the total residence time of the catalyst under DRM conditions without considering the

period of its heating in the methane–carbon dioxide mixture to operating temperature).

TABLE II. GCO stability in dry reforming of methane ($T = 1173\text{K}$)

Sample	Time, h					
	10		20		30	
	$X(\text{CH}_4) / \%$	$X(\text{CO}_2) / \%$	$X(\text{CH}_4) / \%$	$X(\text{CO}_2) / \%$	$X(\text{CH}_4) / \%$	$X(\text{CO}_2) / \%$
GCO _{(NH₄)₂CO₃}	97	99	98	99	97	99
GCO _{NaOH}	96	99	97	99	96	98

The presence of a distinctive 100 % high intensity peak at 2θ 33.90° indicates the production of samples with a perovskite phase. It is worth noting that the use of different precipitators in the synthesis does not affect the width of the peaks and their position on diffractograms, which indicates similar values of crystallite sizes GCO and is confirmed by calculating the average particle diameter using the Scherrer formula (Table III).

TABLE III. S_{BET} , average particle diameter and space group of GCO catalysts

Sample	$S_{\text{BET}} / \text{m}^2 \text{g}^{-1}$	$r_{\text{XRD}} / \text{nm}$	Space group
GCO _{(NH₄)₂CO₃}	6.9	25	Pbnm
GCO _{NaOH}	6.6	25	Pbnm

The calculation of unit cell parameters (Table IV) confirmed that the samples have an orthorhombic crystal lattice ($a \neq b \neq c$) and belong to the space group Pbnm. The calculated parameters of the elementary cells slightly differ from the literature, which indicates some distortion of the crystal lattice; however, the nature of the distortion of the lattice geometry can be associated with the presence of impurity phases, despite their absence in the X-ray spectra, due to the possible low concentration and detection limits of X-ray diffraction analysis.

TABLE IV. Lattice parameters (in nm) of GCO

Sample	a	b	c
GCO _{(NH₄)₂CO₃}	5.161	5.459	7.512
GCO _{NaOH}	5.320	5.419	7.227
Literature (PDF # 00-047-0579)	5.218	5.390	7.445

In such a way, similar conversion and selectivity values may be due to similar structural and texture characteristics of the oxides.

Fig 2b shows diffractograms of samples of GCO_{NaOH} and GCO_{(NH₄)₂CO₃} after catalysis. Under the reaction medium influence, the perovskite phase partially disappears and three additional phases of Gd₂O₃, Gd₂O₂CO₃ and Co are formed. Analysis of literature data¹⁷ suggests that the presence of a carbonate

complex in diffractograms after catalysis of the $\text{Gd}_2\text{O}_2\text{CO}_3$ indicates that the adsorption and the further conversions of carbon dioxide takes place at A-type (Gd) centers. And the appearance of cobalt in a metal state on diffractograms suggests its reduction “from the perovskite structure” with atomic hydrogen formed during the chemisorption of methane in reactions (6) and (7). Fig. 3 demonstrates the chemical property of the DRM process on perovskite-type catalysts.

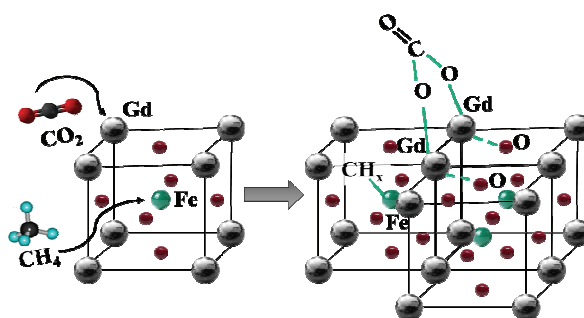
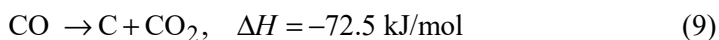


Fig. 3. Illustration of dry reforming of methane reaction.

Analysis of the X-ray diffractograms also showed the presence of carbon on the surface of the test samples, which correlates with the calculation of the carbon balance and indicates the occurrence of side reactions: the methane decomposition (Eq. (7)) and Boudoir reaction:



In addition to the X-ray analysis, the resulting complex oxides were studied by IR spectroscopy.

Fig. 4 shows the IR spectra for the GCO_{NaOH} . The absorption bands corresponding to valence vibrations of Gd–O and Co–O can be observed on the spectrum before catalytic transformations in the region of $500\text{--}700 \text{ cm}^{-1}$ and no reliable signals are observed in the region of $900\text{--}4000 \text{ cm}^{-1}$. On the IR spectrum of the “used-on” surface, the absorption bands were identified in the region of $2800\text{--}3000 \text{ cm}^{-1}$, corresponding to valence vibration of the C–H bond, which are most likely associated with the processes of methane chemisorption on the perovskite surface. The bands at $1900\text{--}2400 \text{ cm}^{-1}$ belong to the Me–CO₂ vibrations and indicate the carbon dioxide adsorption both from the environment and after DRM on the catalyst surface, which is confirmed by XRD data. A wide high intensity band with $\bar{\nu} = 1078 \text{ cm}^{-1}$ is also observed, which corresponds to the valence vibrations of the Si–O bond and is explained by the presence of quartz in the samples used as a substrate. The appearance of bands $3600\text{--}3800 \text{ cm}^{-1}$, corresponding to the valence vibrations of the OH group is due to the presence of adsorbed water, with the intensity of these bands exceeding the values of the

“clean surface” spectrum. Therefore, it can be said that the water is reactive and confirms the progress of the by-process - the reverse water-gas shift reaction.

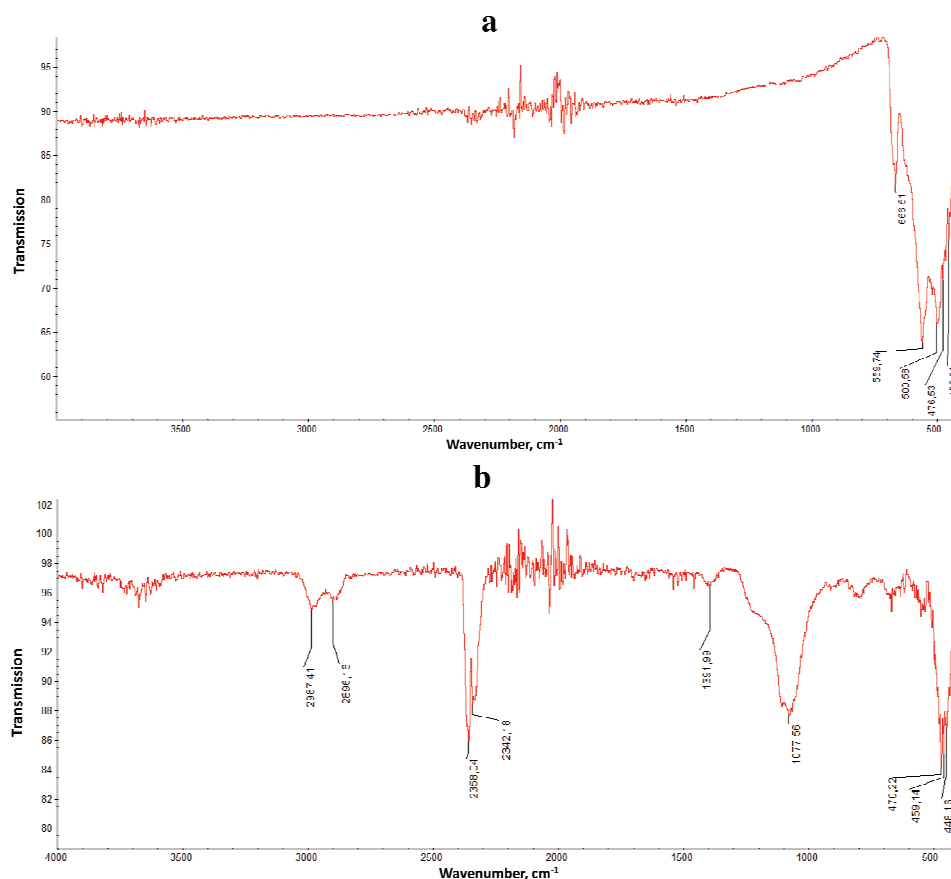


Fig. 4. IR spectra of the GdCoNaOH sample before (a) and after (b) catalysis.

CONCLUSION

It was found that the GdCoO_3 catalyst obtained by the co-precipitation method showed high catalytic activity and stability, regardless of the preparation method. Physical and chemical analysis showed that the choice of precipitant doesn't significantly affect the phase composition of the perovskites and as a consequence on the catalytic performance. The use of gadolinium cobaltites has been shown to inhibit the side reaction of reverse vapour conversion of carbon monoxide. The complex of physicochemical methods of the study revealed that under the reaction medium influence there is a change in the phase composition

of the catalyst sample associated with the appearance of oxycarbonate complexes of gadolinium and the metal phase of cobalt.

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ИЗВОД

СИНТЕЗА, КАРАКТЕРИЗАЦИЈА И КАТАЛИТИЧКЕ ОСОБИНЕ $GdCoO_3$ ЗА СУВО РЕФОРМИСАЊЕ МЕТАНА

REGINA K. ALLABERGENOVA¹, DARIA A. BOBKOVA¹, ELIZAVETA M. BORODINA¹, TATIANA A. KRYUCHKOVA^{1,2}, EKATERINA V. MARKOVA¹, TATIANA F. SHESHKO¹, NIKOLAI N. LOBANOV³
и ALEXANDER G. CHEREDNICHENKO¹

¹Physical and Colloidal Chemistry Department, Faculty of Science, RUDN University, 6 Miklukho-Maklaya St, Moscow, 117198, Russian Federation, ²Moscow Pedagogical State University, MPGU, 1/1 Malaya Pirogovskaya Str., Moscow, 119991, Russian Federation и ³Inorganic Chemistry Department, Faculty of Science, RUDN University, 6 Miklukho-Maklaya St, Moscow, 117198, Russian Federation

Перовскитни оксиди (ABO_3) захваљујући високој термичкој стабилности и могућности контроле физичко–хемијских својстава представљају алтернативу традиционалним катализаторима који садрже племените и прелазне метале. У овом раду су представљени резултати експерименталних истраживања $GdCoO_3$ катализатора. Комплексни оксиди $GdCoO_3$ перовскитног типа добијени методом копреципитације са различитим таложним агенсима карактерисани су применом дифракције X-зрачења (XRD), ниско температурске адсорпције/десорпције азота и ИС спектроскопије. Физичка и хемијска анализа је показала да избор таложног агенса не утиче значајно на фазни састав перовскита. Такође су испитивана каталитичка својства гадолинијум–кобалтита. Показано је да примена кобалтита добијених копреципитацијом доводи до инхибиције споредне реакције реверзибилног реформинга угљен–моноксида. Коначно, испитивањем коришћених катализатора утврђено је да долази до формирања $Gd_2O_2CO_3$ и металног кобалта, што указује на природу активних центара: гадолинијум је центар за CO адсорпцију док се хемисорпција водоника одвија на кобалтним центрима.

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REFERENCES

1. S. V. Razmanova, I. A. Machula, *Oil Gas Geol. Theory Practice* **10** (2015) 37 (https://doi.org/10.17353/2070-5379/38_2015)
2. G. R. S. Santos, O. M. Basha, R. Wang, H. Ashkanani, B. Morsi, *Catal. Today* **371** (2021) 93 (<http://dx.doi.org/10.1016/j.cattod.2020.07.012>)
3. M. M. Nair, S. Kaliaguine, *New J. Chem.* **40** (2016) 4049 (<http://dx.doi.org/10.1039/C5NJ03268G>)
4. W. Y. Kim, J. S. Jang, E. C. Ra, K. Y. Kim, E. H. Kim, J. S. Lee, *Appl. Catal., A* **575** (2019) 198 (<https://doi.org/10.1016/j.apcata.2019.02.029>)
5. K. Sutthiumporn, T. Maneerung, Y. Kathiraser, S. Kawi, *Int. J. Hydrogen Energy* **37** (2012) 11195 (<https://doi.org/10.1016/j.ijhydene.2012.04.059>)
6. E. le Saché, L. Pastor-Pérez, V. Garcilaso, D. J. Watson, M. A. Centeno, J. A. Odriozola, T. R. Reina, *Catal. Today* **357** (2020) 583 (<https://doi.org/10.1016/j.cattod.2019.05.039>)

7. R. Pereniguez, V. M. Gonzalez-delaCruz, A. Caballero, J. P. Holgado, *Appl Catal., B* **123–124** (2012) 346 (<https://doi.org/10.1016/j.apcatb.2012.04.044>)
8. S. Bhattar, M. A. Abedin, S. Kanitkar, J. J. Spivey, *Catal. Today* **365** (2021) 2 (<https://doi.org/10.1016/j.cattod.2020.10.041>)
9. V. V. Kost, T. A. Kryuchkova, V. D. Zimina, T. F. Sheshko, A. G. Cherednichenko, V. V. Kurilkin, M. G. Safronenko, L. V. Yafarova, *Bulg. Chem. Commun.* **51** (2019) 138 (http://www.bcc.bas.bg/BCC_Volumes/Volume_51_Special_D_2019/BCC-51-D-2019-138-142-Kost-29.pdf)
10. T. A. Kryuchkova, T. F. Sheshko, V. D. Zimina, V. V. Kurilkin, Y. M. Serov, I. A. Zvereva, L. V. Yafarova, in *Proceedings of 9th International Conference on Nanomaterials - Research & Application* (2018). TANGER Ltd., Ostrava, Czech Republic, p. 327
11. C. Shi, S. Wang, X. Ge, S. Deng, B. Chen, J. Shen, *J. CO₂ Util.* **46** (2021) 101462 (<https://doi.org/10.1016/j.jcou.2021.101462>)
12. E. V. Dokuchits, A. N. Tafiievich, N. V. Shtertser, T. P. Minyukova, *J. Sib. Fed. Univ.: Chem.* **12** (2019) 177 (<http://dx.doi.org/10.17516/1998-2836-0117>)
13. M. Mousavi and A. N. Pour, *New J. Chem.* **43** (2019) 10763 (<http://dx.doi.org/10.1039/C9NJ01805K>)
14. J. M. Lavoie, *Front. Chem.* **2** (2014) 1 (<http://dx.doi.org/10.3389/fchem.2014.00081>)
15. M. K. Nikoo, N. A. S. Amin, *Fuel Process. Technol.* **92** (2011) 678 (<http://dx.doi.org/10.1016/j.fuproc.2010.11.027>)
16. S. V. Kurgan, G. S. Petrov, L. A. Bashkirov, A. I. Klyndyuk, *Inorg. Mater.* **40** (2004) 1224 (<http://dx.doi.org/10.1023/B:INMA.0000048227.83354.3c>)
17. M. R. Goldwasser, M. E. Rivas, M. L. Lugo, E. Pietri, J. Pérez-Zurita, M. L. Cubeiro, A. Griboval-Constant, G. Leclercq, *Catal. Today* **107–108** (2005) 106 (<http://dx.doi.org/10.1016/j.cattod.2005.07.073>).