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Synthesis of Higher Alcohols on Silver-promoted LaCo- and LaCoCu-Perovskites

Eugene V. Dokuchits* and Tatyana P. Minyukova
*FRC «Boreskov Institute of Catalysis SB RAS»
Novosibirsk, Russian Federation*

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Abstract. LaCoO₃ and LaCo_{0.7}Cu_{0.3}O₃ perovskites supported on highly dispersed mesoporous silica KIT-6 were impregnated with silver nitrate ($n_{Ag}/n_{Co} = 4/99$ and $8/99$). The phase composition of the initial samples and samples after catalytic tests in syngas conversion and catalytic characteristics have been investigated. The regularities of the transformation of samples in the process of reduction in a hydrogen-containing gas have been studied. It is shown that, for the LaCoO₃ sample, with an increase in the silver content, the activity and selectivity for higher alcohols increase from 6 to 23 %. The maximum interaction of cobalt with silver is observed at a silver content of 4 %. At a higher content, part of the cobalt is reduced regardless of the influence of silver due to its faster agglomeration. This leads to a stronger amorphization of the reduced sample and a sharp increase in its activity. The LaCo_{0.7}Cu_{0.3}O₃ sample exhibits a higher selectivity for higher alcohols (36 %) due to the effect of copper. Silver promotion of the sample allows achieving the maximum selectivity for higher alcohols of 56 % with a silver content of 4 %. A further increase in the silver content leads to a sharp decrease in the selectivity for higher alcohols (41 %) and the appearance of CO₂ due to the saturation of copper-containing particles with silver and a decrease in the interaction of cobalt with copper.

Keywords: syngas conversion, synthesis of higher alcohols, silver-promoted La-Co catalysts.

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* Corresponding author E-mail address: oschtan@catalysis.ru

ORCID: 0000-0001-9052-1413 (Dokuchits); 0000-0002-0781-9700 (Minyukova)

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Синтез высших спиртов на LaCo- и LaCoCu-перовскитах, промотированных серебром

Е. В. Докучиц, Т. П. Минюкова

*Институт катализа им. Г. К. Борескова ФИЦ СО РАН
Российская Федерация, Новосибирск*

Аннотация. Перовскиты LaCoO_3 и $\text{LaCo}_{0.7}\text{Cu}_{0.3}\text{O}_3$, нанесенные на высокодисперсный мезопористый кремнезем КИТ-6, пропитывались нитратом серебра ($n_{\text{Ag}}/n_{\text{Co}} = 4/99$ и $8/99$). Исследован фазовый состав исходных образцов и образцов после каталитических испытаний в конверсии синтез-газа и каталитические характеристики образцов. Изучены закономерности превращения образцов в процессе восстановления в водородсодержащем газе. Показано, что для образца LaCoO_3 с ростом содержания серебра увеличивается активность и селективность по высшим спиртам с 6 до 23 %. Максимальное взаимодействие кобальта с серебром наблюдается при содержании 4 % серебра. При большем содержании часть кобальта восстанавливается независимо от влияния серебра вследствие его более быстрой агломерации. Это приводит к более сильной аморфизации восстановленного образца и резкому росту его активности. Образец $\text{LaCo}_{0.7}\text{Cu}_{0.3}\text{O}_3$ проявляет более высокую селективность по высшим спиртам (36 %) благодаря влиянию меди. Промотирование образца серебром позволяет достичь максимальной селективности по высшим спиртам в 56 % при содержании серебра в 4 %. Дальнейшее увеличение содержания серебра приводит к резкому снижению селективности по высшим спиртам (41 %) и появлению CO_2 вследствие насыщения медьсодержащих частиц серебром и снижению взаимодействия кобальта с медью.

Ключевые слова: конверсия синтез-газа, синтез высших спиртов, промотированные серебром La-Co-катализаторы.

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1. Introduction

Conversion of syngas obtained via the processing of biomass or conversion of carbon dioxide [1, 2, 3] into various valuable chemical products (hydrocarbons, higher alcohols) will make it possible to abandon the use of natural fuel. Cobalt catalysts are the most effective for the conversion of syngas. Promotion of cobalt-containing catalysts is an important way of their modification in order to significantly reduce the reduction temperature, increase the activity, and control the selectivity for higher hydrocarbons and alcohols. The conventional promoters of these catalysts are expensive noble metals [4]. At the same time, in recent years, the possibility of using cheaper metals as promoters of cobalt-containing catalysts has been actively studied. Promotion with Group 11 metals (Cu, Ag, Au) is considered as the most promising replacement for precious metals. The most effective among these metals is Ag, which provides a significant increase in the activity of catalysts with Ag content increase compared to Au and Cu [5]. It can be explained by the formation of a larger amount of the metastable β -Co phase with a hexagonal close-packed lattice during reductive activation in an Ag-containing catalyst [6]. In this case, a high content of Cu and Au leads to a decrease in the activity of the catalyst, which is caused by the coating of the edges of cobalt clusters with a promoter [5]. Silver has a fundamentally different atomic structure in comparison with copper, gold and platinum, and promotion with silver has little effect on selectivity, but a significant content leads to a decrease in activity [7].

It was shown with DFT method [8], that the rate of syngas conversion over Co-containing catalysts is controlled by CO dissociation and oxygen removal through the formation of water. Silver promotion of the cobalt surface decreases the rate of structure-sensitive CO dissociation and structure-sensitive reaction of subsequent hydrogenation. It leads to a longer lifetime of the intermediate CH_x compounds and, accordingly, to an increase in the probability of chain growth. In this case, the rate of oxygen removal in the presence of silver increases [9]. It has been shown [10] that the process of oxygen hydrogenation on silver includes a fast stage of the formation of adsorbed hydroxyl groups, which are then slowly removed in the form of water. It can be assumed that, in the case of the formation of silver clusters on the surface of cobalt clusters, silver can both facilitate the incorporation of an associatively adsorbed CO molecule into CH_x -Co followed by hydrogenation and lead to termination of the CH_x -Co chain. In both cases, an increase in selectivity to alcohols will be observed.

A combination of Ag and other metals promotion of Co-containing catalysts may give an interesting result. Thus, promotion with lanthanum [11] improves the overall reducibility of cobalt and the surface area of the cobalt, which leads to an increase in the overall catalytic activity. Introduction of lanthanum into the catalytic system makes it possible to suppress the formation of carbon dioxide, as in the case of the Fe-Cu-La sample [12] and perovskite $\text{LaCo}_{0.7}\text{Ni}_{0.3}\text{O}_3$ [13]. It turns out to be important in the case of the promotion of a cobalt-containing catalyst with copper, which, together with the presence of lanthanum, leads to a significant increase in the selectivity for higher alcohols [14, 15]. In this case, copper-containing catalysts are conventional catalysts for a water-gas shift reaction, which inevitably leads to CO_2 formation.

In the present paper, we studied the effect of silver promotion of oxide precursors LaCoO_3 and $\text{LaCo}_{0.7}\text{Cu}_{0.3}\text{O}_3$ of a perovskite-type structure, supported on KIT-6 silica, on the activity and selectivity for higher alcohols in the conversion of syngas. It was proposed, that the inclusion of lanthanum,

cobalt, and copper cations in the perovskite structure would ensure their strong interaction at the stage of sample reduction and provide the best synergistic effect.

2. Experimental

The oxide samples were synthesized with the citrate method by mixing metal nitrates, citric acid, water, alcohol, and KIT-6 silica, described elsewhere [16]. KIT-6 silica was partially removed by leaching in NaOH solution [17]. The synthesized samples were characterized by chemical analysis (Optima 4300 DV, Perkin Elmer), X-ray diffraction (D8, Bruker), and thermal analysis (Netzsch STA 409) in an Ar + H₂ mixture (1/1). The resulting finely dispersed samples were divided into 3 portions, two of them were impregnated with an aqueous solution of silver nitrate based on the atomic ratio Ag/Co = 4/99 and 8/99 according to the established cobalt content in the sample. Then the samples were dried in air in a place protected from direct sunlight with occasional thorough mixing.

Catalytic tests with a duration of 18–19 h were performed in a periodic mode in a flow laboratory reactor at a temperature of 240 °C, a pressure of 2 MPa, and the following gas composition: CO/H₂ = 1/2 and 10 % nitrogen (an internal standard). A powder with a grain size of 0.14–0.25 mm was prepared from the sample. The reductive activation of the samples before catalytic measurements was carried out in a flow of an H₂/Ar mixture at temperature 500 °C for LaCoO₃ sample and 330 °C for LaCo_{0.7}Cu_{0.3}O₃ sample, based on the results of DTA. GHSV was selected in such a way that CO conversion was not high and close for all the samples, that is, the tests took place under similar conditions. The composition of the gaseous products was analyzed continuously. Liquid products were collected and analyzed after the reaction.

3. Results and discussion

According to XRD data, the synthesized samples LaCoO₃/KIT-6 и LaCo_{0.7}Cu_{0.3}O₃/KIT-6 consist of a phase with a perovskite structure with a rhombohedral lattice R $\bar{3}c$ (LaCoO₃ – ICDD PDF2 00–048–0123) (Fig. 1). It should be noted that the samples consist of only one phase; no cobalt or copper oxides are observed.

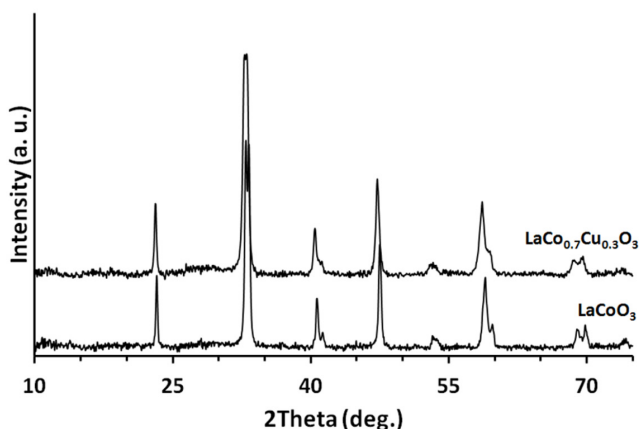


Fig. 1. Diffraction patterns of initial samples LaCoO₃/KIT-6 and LaCo_{0.7}Cu_{0.3}O₃/KIT-6. All reflexes belong to the perovskite phase

The transformations during reductive activation were investigated by thermal analysis. According to thermal analysis in the Ar+H₂ mixture data (Fig. 2) for all samples, a weight loss effect is observed in the region of 130 °C, corresponding to the removal of adsorbed water. In the case of LaCoO₃ reduction, three exothermic effects are observed: 357, 478, and 677 °C. The first two peaks refer to sequential cobalt reduction: Co³⁺ → Co²⁺ and Co²⁺ → Co⁰ [18]. The mass loss values for these two stages of cobalt reduction turn out to be close, although they should correlate as 1/2. The close value of the weight loss with a thermal effect of 677 °C indicates that this effect is related to the reduction of a part of the cobalt at this temperature. An increase in the temperature of Co²⁺ reduction to 677 °C may be due to the influence of the support, which leads to the formation of hardly reducible cobalt silicate Co₂SiO₄ [19]. Promotion of LaCoO₃ with silver nitrate slightly changes the pattern of cobalt reduction. The main effect is traced in a decrease in the temperature of the first stage of reduction of cobalt Co³⁺ → Co²⁺ and its prolongation. In this case, an increase in the silver content leads to a stronger shift towards lower temperatures. The second thermal effect during the promotion of LaCoO₃ with silver also shifts somewhat to the region of lower temperatures. It can be assumed that the optimal silver content, at which the maximum interaction of cobalt with silver is ensured, is located near the n_{Ag}/n_{Co} = 4/99 region, which is consistent with the data of other authors. [5]. In the samples promoted with silver, some of the Co²⁺ cations are also reduced at temperatures above 600 °C due to the formation of cobalt silicate, which is a result of the deep interaction of the perovskite phase with KIT-6 silica and its partial incorporation into the perovskite structure [16].

A similar picture is observed for the LaCo_{0.7}Cu_{0.3}O₃ samples. Most of the cations of cobalt and copper are reduced together at a temperature of 266 °C with the formation, probably, of bimetallic

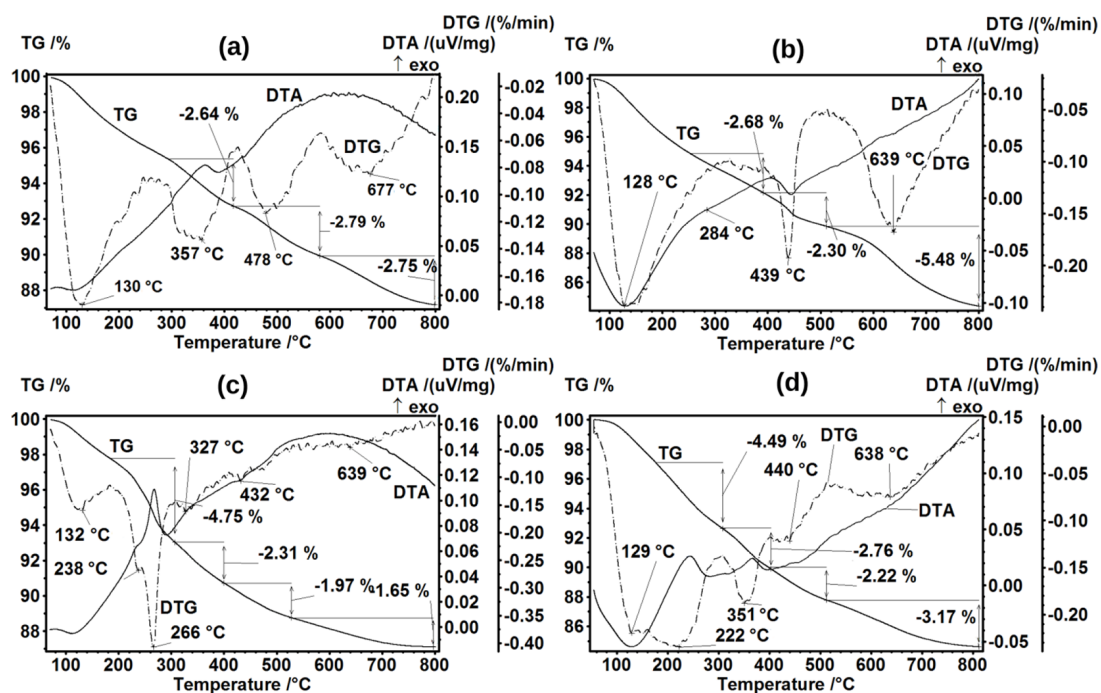


Fig. 2. DTA data of samples in a hydrogen-containing mixture: (a) LaCoO₃/KIT-6, (b) 4 %Ag/LaCoO₃/KIT-6, (c) LaCo_{0.7}Ti_{0.3}O₃/KIT-6, (d) 4 %Ag/LaCo_{0.7}Ti_{0.3}O₃/KIT-6

Cu-Co particles. However, some of the copper and cobalt cations are reduced separately: for copper cations – 238 °C; for cobalt cations – 327, 432, 639 °C. The reduction temperatures of cobalt cations are close to the reduction temperatures in the case of the silver-promoted LaCoO₃ sample. The separate reduction of cobalt and copper cations is apparently related to the cations located on the surface of the perovskite phase. A low proportion of separately reducible cobalt cations leads to a weakly pronounced thermal effect of the reduction of cobalt at temperatures above 600 °C caused by the formation of cobalt silicate. The promotion of copper-containing perovskite with silver significantly changes the nature of the reduction of the samples. So, in the case of a silver content of 4 %, the reduction of copper with cobalt starts at a temperature of less than 200 °C with a maximum at 222 °C. Thermal effects are observed corresponding to the separate reduction of some of the cobalt cations: 351, about 440 and 638 °C. Probably due to the close surface tension [20] of copper and silver, a similar crystal lattice (Fm $\bar{3}$ m) and the possibility of the formation of binary alloys of any composition [21] silver modifies the surface of the formed Cu-Co particles with suppression of the complete reduction of cobalt. With a further increase in the silver content (8 %), in addition to the analogous stage of the combined reduction of copper with cobalt, thermal effects of the separate reduction of cobalt from copper are also observed. In this case, the first stage of cobalt reduction occurs at a temperature of about 300 °C. We believe that the maximum silver content that can be associated with the forming Cu-Co particles in this system is in the range from 4 % to 8 %. With a further increase in the silver content to 8 %, some of the silver is unbound with such particles and can affect the reduction of the remaining cobalt cations, lowering the observed reduction temperature, similar to the reduction of cobalt in the 4 %Ag/LaCoO₃ sample.

According to the observed regularities of the reduction of samples with hydrogen, one should expect that in the case of the separate reduction of cobalt cations from the reduction of silver and copper, in addition to the particles of cobalt modified by copper and / or silver, an unmodified cobalt particles will also appear. Such samples should have a higher activity in syngas conversion. This is due to the fact that silver on the surface of cobalt particles occupies the most active centers, reducing the overall activity of such particles, while, however, contributing to an increase in the selectivity for alcohols, an increase in the chain length, and a decrease in the selectivity for light hydrocarbons [9]. To reduce the samples, a temperature was chosen that ensures the complete reduction of cobalt, with the exception of the forming phase of cobalt silicate. It was 500 °C for samples based on LaCoO₃ and 330 °C for samples based on LaCo_{0.7}Cu_{0.3}O₃.

The results of catalytic tests of the samples in syngas conversion are consistent with the assumption made above. Thus, in the case of LaCoO₃, with an increase in the silver content, the activity and selectivity for alcohols increases significantly (Table 1) with a simultaneous decrease in the selectivity for paraffins. The constant value of the distribution parameter of alcohols α indicates that CH_x hydrocarbon particles are formed on cobalt particles, and silver clusters are responsible for their termination by the introduction of an associatively adsorbed CO molecule. Correspondingly, with an increase in the silver content, the selectivity for alcohols increases. The fraction of alcohols is represented in the overwhelming majority of primary alcohols, which excludes the possibility of their synthesis by hydration of olefins.

In the case of the LaCo_{0.7}Cu_{0.3}O₃ sample, the promotion with silver decreases the activity of the samples, probably due to a decrease in the activity of copper-containing metal particles, including the

Table 1. Catalytic properties of samples on mesoporous silica KIT-6 in the syngas conversion at pressure of 2 MPa and 240 °C and gas composition $H_2/CO = 2/1$

Sample	n_{Ag}/n_{Co}	S_{sa} , m^2/g	GHSV, h^{-1}	X_{CO} , %	S_{CO_2} , %	S_{CH_4} , %	$S_{C_{2+}}$, %	ROH, C _{1–6}			RH, C _{9–16}			
								S , %	α_{ASF}	Y	α_{ASF}	S , %	Y	en/an
LaCoO ₃	-	117	2350	22.4	0	18.7	14.9	6.1	0.41	9	0.82	60.6	52	0.21
4 %Ag/LaCoO ₃	4/99	- ^a	2480	24.8	0	17.1	11.6	13.0	0.39	25	0.83	58.3	64	0.12
8 %Ag/LaCoO ₃	8/99	- ^a	3340	22.5	0	19.0	12.2	23.2	0.40	57	0.81	45.6	205	0.11
LaCo _{0.7} Cu _{0.3} O ₃	-	193	1320	19.3	0	21.1	13.7	36.4	0.40	24	0.78	28.8	15	0.08
4 %Ag/LaCo _{0.7} Cu _{0.3} O ₃	4/99	- ^a	940	15.4	0	20.8	13.3	55.8	0.39	21	0.78	10.1	2	0.13
8 %Ag/LaCo _{0.7} Cu _{0.3} O ₃	8/99	- ^a	1060	18.5	2.1	17.3	12.8	41.4	0.40	24	0.79	26.4	9	0.11

^a – the specific surface area was not measured for the samples impregnated with silver nitrate, since the method requires a thermal pretreatment, which can cause changes in the texture of the samples that are difficult to identify.

Table designations: S_{sa} – specific surface area of samples; *GHSV* – gas hourly space velocity (h^{-1}); S – selectivity of CO consumption for the corresponding reaction products (%); X – conversion of CO (%); ROH – alcohols; RH – paraffins; Y – is the yield of product ($mg/g_{cat} \cdot h$); α_{ASF} – the Anderson-Schultz-Flory parameter (α_{2-5} for alcohols, α_{11-20} for paraffins); en/an – olefin to paraffin ratio.

formation of bimetallic Ag-Cu particles. In this case, the distribution parameter of alcohols for copper-containing samples is similar to samples based on LaCoO₃, which also indicates the formation of CH_x particles on cobalt particles, followed by the introduction of a CO molecule associatively adsorbed on copper or silver into CH_x-Co, followed by hydrogenation.

The selectivity for methane and light hydrocarbons for all samples weakly depends on the sample composition. The alcohol selectivity for silver-promoted LaCoO₃ samples increases with increasing silver content. In the case of samples based on LaCo_{0.7}Cu_{0.3}O₃, the alcohol selectivity reaches a maximum at a silver content of 4 %, and at 8 % it significantly decreases due to the binding of all cobalt and copper to silver clusters. In this case, the promotion of cobalt with copper provides a significant increase in the selectivity for higher alcohols and, probably, in the case of the introduction of silver on the 4 %Ag/LaCo_{0.7}Cu_{0.3}O₃ sample, reaches its maximum values. This allows us to consider this sample as the most promising for the synthesis of higher alcohols by syngas conversion.

The high silver content in the sample of 8 %Ag/LaCo_{0.7}Cu_{0.3}O₃ leads to the appearance CO₂ in the products of syngas conversion, that may be caused by a decrease in the strength of interaction between copper and cobalt due to the effect of silver, as indicated in the results of thermal analysis. The ratio of olefins to paraffins for all samples modified with silver is similar, but lower in comparison with the unpromoted sample of LaCoO₃, indicating that silver inhibits the activity of β -hydride elimination centers leading to the formation of olefins.

The results of XRD analysis of the samples after catalytic measurements (Fig. 3) show that all samples contain lanthanum oxide La₂O₃ (ICDD PDF2 01–073–2141), lanthanum hydroxide La(OH)₃ (ICDD PDF2 01–083–2034), cobalt carbide Co₂C (ICDD PDF2 00–050–1371), metallic silver (ICDD PDF2 01–087–0717), a trace amount of cobalt silicate Co₂SiO₄ (ICDD PDF2 00–029–0506) and metallic cobalt. Cobalt metal can be present as a hexagonal-packed α -Co phase (ICDD PDF2 00–005–0727) or as a cubic-packed β -Co phase (ICDD PDF2 00–015–0806). The type of the metallic cobalt phase cannot be accurately determined due to the low intensity of the reflections in the X-ray diffraction pattern and due to the proximity of the (220) α -Co and (111) β -Co reflections. The absence

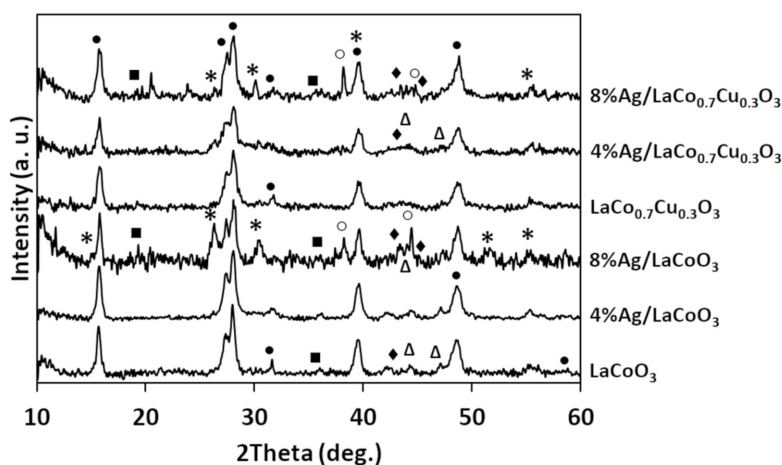


Fig. 3. Diffraction patterns of samples after catalytic tests. Designations: ● – $\text{La}(\text{OH})_3$, * – La_2O_3 , ■ – Co_2SiO_4 , ○ – Ag, ◆ – Co_2C , Δ – Co

of the perovskite phase indicates complete destruction of the samples during reduction and catalytic tests. The low content of cobalt carbide, which is considered to be responsible for the synthesis of alcohols [14, 15], in the samples may be due to both the effect of promoters: silver and copper, which slow down the rate of CO dissociation, and the effect of the lanthanum-containing oxide support. Cobalt silicate suggested on the basis of thermal analysis data is observed in trace amounts, which is well explained by the high amorphization of the samples after catalytic tests. The copper oxide phase is not observed, it may be the result of the formation of bimetallic particles with cobalt on its basis. Reflections of metallic silver are observed only in samples containing 8 % silver, which is in excellent agreement with the thermal analysis data.

4. Conclusions

Silver promotion of perovskite-type oxide precursors LaCoO_3 and $\text{LaCo}_{0.7}\text{Cu}_{0.3}\text{O}_3$, supported on mesoporous silica KIT-6, makes it possible to increase significantly the selectivity of catalysts based on them for higher alcohols in syngas conversion. In the case of LaCoO_3 , the alcohol selectivity increases with an increase in the silver content from 6 to 23 %. Cobalt promotion with copper provides a more significant increase in the selectivity for higher alcohols, and in the case of additional promotion with silver on the 4 %Ag/ $\text{LaCo}_{0.7}\text{Cu}_{0.3}\text{O}_3$ sample, the selectivity reaches a maximum of 56 % with respect to converted CO. In the presence of silver, the reduction temperature of cobalt and copper decreases, while the activity of copper-containing samples decreases. In the case of samples based on LaCoO_3 , with an increase in the silver content, its stronger interaction with a part of the initially reduced cobalt is observed, which probably leads to the formation of a part of cobalt unbound with silver and its independent reduction. This in turn significantly increases the activity of the catalyst. The promotion of cobalt-containing catalysts with silver apparently suppresses the activity of the centers responsible for the synthesis of olefins; their content in hydrocarbons does not exceed 10–12 % of the mass.

The high activity and low commercial price of silver in comparison with other noble metals makes it possible to consider silver as the most promising promoter of catalysts for the synthesis of higher alcohols in syngas conversion.

References

1. Roy P.S., Song J., Kim K., Park C.S., Raju A.S.K. CO₂ conversion to syngas through the steam-biogas reforming process. *Journal of CO₂ Utilization* 2018. Vol. 25, P. 275–282. <https://doi.org/10.1016/j.jcou.2018.04.013>
2. Jeffrey L., Ong M. Y., Nomanbhay S., Mofijur M., Mubashir M., Show P.L. Greenhouse gases utilization: A review. *Fuel* 2021. Vol. 301, P. 121017. <https://doi.org/10.1016/j.fuel.2021.121017>
3. Bahmanpour A. M., Signorile M., Krocher O. Recent progress in syngas production via catalytic CO₂ hydrogenation reaction. *Applied Catalysis B: Environmental* 2021. Vol. 295, P. 120319. <https://doi.org/10.1016/j.apcatb.2021.120319>
4. Diehl F., Khodakov A. Y. Promotion of Cobalt Fischer-Tropsch Catalysts with Noble Metals: a Review. *Oil and Gas Science and Technology* 2009. Vol. 64(1), P. 11–24. <https://doi.org/10.2516/ogst:2008040>
5. Jacobs G., Ribeiro M. C., Ma W., Ji Y., Khalid S., Sumodjo P.T.A., Davis B.H. Group 11 (Cu, Ag, Au) promotion of 15 %Co/Al₂O₃ Fischer–Tropsch synthesis catalysts. *Applied Catalysis A: General* 2009. Vol. 361(1–2), P. 137–151. <https://doi.org/10.1016/j.apcata.2009.04.007>
6. Eschemann T. O., Oenema J., De Jong K. P. Effect of noble metal promotion for Co/TiO₂ Fischer-Tropsch catalysts. *Catalysis Today* 2016. Vol. 261, P. 60–66. <https://doi.org/10.1016/j.cattod.2015.06.016>
7. Jermwongratanachai T., Jacobs G., Maa W., Shafer W. D., Gnanamani M. K., Gao P., Kitiyanan B., Davis B. H., Klettlinger J. L.S., Yen C. H., Cronauer D. C., Kropf A. J., Marshall C. L. Fischer–Tropsch synthesis: Comparisons between Pt and Ag promoted Co/Al₂O₃ catalysts for reducibility, local atomic structure, catalytic activity and oxidation-reduction (OR) cycles. *Applied Catalysis A: General* 2013. Vol. 464–465, P. 165–180. <https://doi.org/10.1016/j.apcata.2013.05.040>
8. Pilot I. A.W., Van Santen R. A., Hensen E. J.M. The Optimally Performing Fischer–Tropsch Catalyst. *Angewandte Chemie International Edition in English* 2014. Vol. 53(47), P. 12746–12750. <https://doi.org/10.1002/anie.201406521>
9. Chen W., Pestman R., Chiang F.-K., Hensen E. J.M. Silver addition to a cobalt Fischer–Tropsch catalyst. *Journal of Catalysis* 2018. Vol. 366, P. 107–114. <https://doi.org/10.1016/j.jcat.2018.07.028>
10. Dokuchits E. V., Khasin A. V., Khassin A. A. Mechanism of the Catalytic Synthesis of Water on Silver. *Mendeleev Communication* 2015. Vol. 25(2), P. 155–156. <http://doi.org/10.1016/j.mencom.2015.03.028>
11. Shimura K., Miyazawa T., Hanaoka T., Hirata S. Fischer–Tropsch synthesis over alumina supported cobalt catalyst: Effect of promoter addition. *Applied Catalysis A: General* 2015, Vol. 494, P. 1–11. <https://doi.org/10.1016/j.apcata.2015.01.017>
12. Barama A., Bettahar M.M., Kiennemann A. Higher alcohol synthesis on iron-copper-molybdenum containing catalysts. *Studies in Surface Science and Catalysis* 1997. Vol. 107, P. 47–54. [https://doi.org/10.1016/S0167-2991\(97\)80315-1](https://doi.org/10.1016/S0167-2991(97)80315-1)
13. Tsoukalou A., Imtiaz Q., Kim S.M., Abdala P.M., Yoon S., Müller C. R. Dry-reforming of methane over bimetallic Ni–M/La₂O₃ (M = Co, Fe): The effect of the rate of La₂O₂CO₃ formation and phase stability on the catalytic activity and stability. *Journal of Catalysis* 2016. Vol. 343, P. 208–214. <https://doi.org/10.1016/j.jcat.2016.03.018>

14. Ao M., Pham G. H., Sunarso J., Li F. P., Jin Y., Liu S. M. Effects of alkali promoters on trimetallic Co-Ni-Cu-based perovskite catalyst for higher alcohol synthesis from syngas. *Catalysis Today* 2020. Vol. 355(Si), P. 26–34. <https://doi.org/10.1016/j.cattod.2019.06.061>

15. Gobel C., Schmidt S., Froese C., Fu Q., Chen Y. T., Pan Q. S., Muhler M. Structural evolution of bimetallic Co-Cu catalysts in CO hydrogenation to higher alcohols at high pressure. *Journal of Catalysis* 2020. Vol. 383, P. 33–41. <https://doi.org/10.1016/j.jcat.2020.01.004>

16. Dokuchits E. V., Larina T. V., Gerasimov E. Yu., Pochtar A. A., Minyukova T. P. Syngas conversion over perovskite-like $\text{LaCu}_x\text{Ti}_{1-x}\text{O}_3$ /KIT-6 catalysts. *Applied Catalysis A: General* 2020. Vol. 608, P. 117834. <https://doi.org/10.1016/j.apcata.2020.117834>

17. Wang Y., Ren J., Wang Y., Zhang F., Liu X., Guo Y., Lu G. Nanocasted Synthesis of Mesoporous LaCoO_3 Perovskite with Extremely High Surface Area and Excellent Activity in Methane Combustion. *The Journal of Physical Chemistry C* 2008. Vol. 112(39), P. 15293–15298. <https://doi.org/10.1021/jp8048394>

18. Prado-Gonjal J., Gutierrez-Seijas J., Anzorregui I. H., Moran E., Terry I., Schmidt R. The role of defects in microwave and conventionally synthesized LaCoO_3 perovskite. *Journal of the European Ceramic Society* 2016, Vol. 36(5), P. 1197–1206. <https://doi.org/10.1016/j.jeurceramsoc.2015.12.014>

19. Khassin A. A., Yutieva T. M., Kustova G. N., Plyasova L. M., Itenberg I. Sh., Demeshkina M. P., Chermashentseva G. K., Anufrienko V. F., Zaikovski V. I., Larina T. V., Molina I. Yu., Parmon V. N. Cobalt-containing catalysts supported by synthetic Zn- and Mg-stevensites and their performance in the Fischer–Tropsch synthesis. *Journal of Molecular Catalysis A: Chemical* 2001. Vol. 168(1–2), P. 209–224. [https://doi.org/10.1016/S1381-1169\(00\)00530-6](https://doi.org/10.1016/S1381-1169(00)00530-6)

20. Jurov V. M., Laurinas V. Ch., Guchenko S. A., Zavatskaja O. N. Dimensional effects and superficial tension of pure metals. *Advances in current natural sciences* 2012. Vol. 7, P. 88–93. <http://www.natural-sciences.ru/ru/article/view?id=30295>

21. Диаграммы состояния двойных металлических систем. Под ред. Н. П. Лякишева. М.: Машиностроение, 1996, с. 34–38. [State diagrams of binary metal systems. Under ed. N. P. Lyakishev. Moscow: Mashinostroyeniye, 1996, P. 34–38. (In Russ.)]