Research Article

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$LaCoO_3$ perovskite-type catalysts in syngas conversion

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Abstract: $LaCoO_3$ samples were obtained by the hydrothermal and citrate methods. The dynamics of the phase transformations of the initial hydroxo compounds into the oxide state and the subsequent reduction in a hydrogen-containing mixture were studied by the differential thermal analysis and X-ray diffraction methods. The results of the catalytic tests in the syngas conversion showed that the path of conversion depends on the phase composition of the catalyst in the oxide state. In contrast to the standard CoAl sample, alcohols prevail in the liquid products formed on $LaCoO_3$ catalysts.

Keywords: synthesis gas transformation, synthesis of alcohols

1 Introduction

One of the processes for producing synthetic liquid fuel and valuable chemical compounds based on non-petroleum feedstock (coal, natural gas, and biomass) is the synthesis of hydrocarbons and alcohols from syngas, proceeding with the participation of catalysts containing various transition metals [1–4]. Currently, much attention is paid to the selective conversion of syngas, in particular, the synthesis of linear hydrocarbons, solid linear paraffins (Fischer–Tropsch synthesis), and alcohols [5], which requires the development of catalysts with not only high activity and stability but also high selectivity with respect to the formation of certain hydrocarbon products. Application of perovskite-like oxides for these purposes is very promising [6], due to their high activity, stability, selectivity, and low cost.

There are several approaches to the preparation of catalysts with a high specific surface area based on the oxides of a perovskite structure. One of the possible ways is to fix the active component on the surface of an inert oxide or to introduce it into ceramic/cermet foamy supports [7]. Another method to obtain the sample of a high specific surface area is template synthesis, which includes the use of a high surface area template at the precursor compound formation stage [8].

This work is devoted to study the physicochemical and catalytic properties of the perovskite-type mixed $LaCoO_3$ oxide synthesized by two ways: hydrothermal method, using ethylene glycol, and citrate method, using mesoporous silica KIT-6. The catalytic behavior of the synthesized samples differs from that of the reference CoAl Fischer–Tropsch synthesis catalyst, prepared by the method described in [9]. $LaCoO_3$/KIT-6 catalyst has a higher activity and selectivity toward higher alcohols than the bulk ones.

2 Methods

2.1 Catalyst preparation

The following reagents were used in this study: $La(NO_3)_3 \cdot 6H_2O$ (chemically pure, Reakhim, TU 6-09-4676-83), $Co(NO_3)_2 \cdot 6H_2O$ (pure, Reakhim, GOST 4528-78), NaOH (chemically pure, Ekros, GOST 4328-77), HNO_3 (ultrapure, GOST-11125-84), ethylene glycol (chemically

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pure, Reakhim, GOST 19710-83), KIT-6 (ASC Material), citric acid (chemically pure, Ekros, GOST 36-52-69), and C_2H_5OH (Reakhim, GOST R 51999-2002).

Two $LaCoO_3$ samples with different La:Co ratios were obtained by the hydrothermal method [10] in the presence of ethylene glycol. To obtain the first sample, LCO-1, 6 cmol of lanthanum nitrate and 6 cmol of cobalt nitrate were dissolved in 80 mL of water at room temperature. Then, 16 cmol of ethylene glycol was added to the solution and 120 mL of a 4 M sodium hydroxide solution was added next. The required amount of nitric acid was added to the above solution until pH = 10 was reached, and the solution was kept under stirring for 2 h. Then, the resulting suspension was kept in a closed vessel for 24 h at 100°C. The precipitate was washed on a filter paper with 5 L of distilled water and dried under an infrared lamp. After grinding, the obtained powder was successively calcined in air at 500°C for 3 h and then at 750°C for 4 h.

The second sample, LCO-2, was obtained in a similar way, and the amount of metal cations in this synthesis was 6 cmol of lanthanum and 8 cmol of cobalt. This ratio was chosen on the basis of the work of Kungurova et al. [9], affirming the possible incompleteness of cobalt precipitation under the synthesis conditions.

$LaCoO_3$/KIT-6 (LCO/KIT-6) sample was obtained by the citrate method. In this case, 6 g of the mesoporous silica support KIT-6 [11] was suspended in 60 mL of distilled water, then 0.03 mol of cobalt nitrate, 3 cmol of lanthanum nitrate, 60 mL of ethanol, and 23.5 g of citric acid were added. Then, the suspension was slowly evaporated under continuous stirring at a temperature of 75°C until a thick gel was formed. The gel was dried at 90°C for 12 h and ground into powder. The obtained powder was subjected to heat treatment similar to that of the first two samples. Then, the main amount of KIT-6 silica was removed from the sample by dissolving it in 500 mL of a 7% NaOH solution at 75°C for 15 min. Then, the sample was filtered, washed on a filter paper with 8 L of distilled water at 75°C, and dried at 90°C.

2.2 Physicochemical studies

Chemical analysis of the cationic composition of the samples was carried out by the atomic emission spectroscopy with an Optima 4300 DV instrument from PerkinElmer.

The total accessible surface of the samples was calculated by the BET method using nitrogen adsorption isotherms obtained on an ASAP-2400 device from Micrometrics (USA) after training samples in a vacuum at 150°C.

The phase composition of the samples was determined by the X-ray diffraction (XRD) analysis on a D-8 diffractometer (Bruker) using Cu-Kα radiation by point scanning with an interval of 0.05° in the 2θ angle range from 20° to 80°.

To determine the thermal treatment conditions, thermal analysis (TA) of the dry and calcined samples was performed in air and in a flow of argon and hydrogen mixture (40 mL/min) at a heating rate of 10 K/min and 5 K/min, respectively. The study was performed on a Netzsch STA-409 thermograph.

Catalytic tests of the samples were performed on a Fischer–Tropsch synthesis setup under the following conditions: composition of the initial working mixture $CO:H_2:N_2$ was 3:6:1 (nitrogen as an internal standard), the mixture flow rate was 1 L/h, samples of 0.14/0.25 mm fraction were used, gas hour space velocity (GHSV) was 450/1000 h^{-1}, temperature 240°C, and pressure 2 MPa. Before testing, the catalyst was activated in a hydrogen-containing mixture at 520°C. The temperature was selected based on the TA in a hydrogen-containing mixture. Selectivity was calculated as the portion of converted CO spent on a specific reaction product. For the target product groups (alcohols and higher paraffins), the Anderson–Schulz–Flory (α_{ASF}) parameter of the distribution of products along the chain length was calculated. A CoAl catalyst prepared according to the patent [12] was tested as a reference sample.

Ethical approval: The research conducted is not related to either human or animal use.

3 Results and discussion

According to the results of the chemical analysis (Table 2), the content of lanthanum and cobalt in all the samples

Table 1: Observed thermal effects for the precursor sample LCO-1 in air

Temperature, °C	Intended process	Ref.
<150	Desorption of water	—
204	$12Co(OH)_2 + 2O_2 \rightarrow 4Co_3O_4 + 12H_2O$	[13]
204–345	$5CoCO_3 \cdot Co(OH)_2 + O_2 \rightarrow 2Co_3O_4 + 5CO_2 + 5H_2O$	[14]
345	$La(OH)_3 \rightarrow LaOOH + H_2O$	[15]
500–600	$2La(OH)CO_3 \rightarrow La_2O_2CO_3 + H_2O + CO_2$	[16]
	$12LaOOH + 4Co_3O_4 + O_2 \rightarrow 12LaCoO_3 + 6H_2O$	[15]

Table 2: Results of the catalytic tests in the syngas conversion at a pressure of 2 MPa. *S* is the selectivity of CO consumption for the corresponding reaction products, *X* is the conversion of CO, *Y* is the yield of alcohols, α_{ASF} is the Anderson–Schulz–Flory parameter

	LCO-1	LCO-2	LCO/KIT-6	CoAl
Chemical composition, wt%	La – 49.5 Co – 21.1 Na – 0.05	La – 50 Co – 28.6 Na – 0.06	La – 51.9 Co – 22 Na – 0.05 Si – 8.1	—
Reaction temperature, °C	240			210
GHSV, h^{-1}	1,000	590	450	2,440
Gas flow rate, L/h	1.0	1.0	1.0	4.7
S, m^2/g	9.5	10	220	116
d_{pores}, Å	37	23	12	15
X_{CO}, %	17	20	60	20
S_{CO_2}, %	6	3	3	0
S_{CH_4}, %	3	36	9	6
$S_{C_2-C_8}$, %	1	19	7	5
S_{ROH}, %	90	42	61	22
α_{ASF}, alcohols (ROH)	0.32	0.32	0.43	0.46
Y_{ROH}, $mg/g_{cat}{\cdot}h$	57	21	80	72
$S_{paraffins}$, %	0.2	<0.1	20	67
α_{ASF}, paraffins, C_{9-23}	0.78	0.78	0.79	0.81
w_{H_2O}, % in alcohols fraction	17	49	26	76

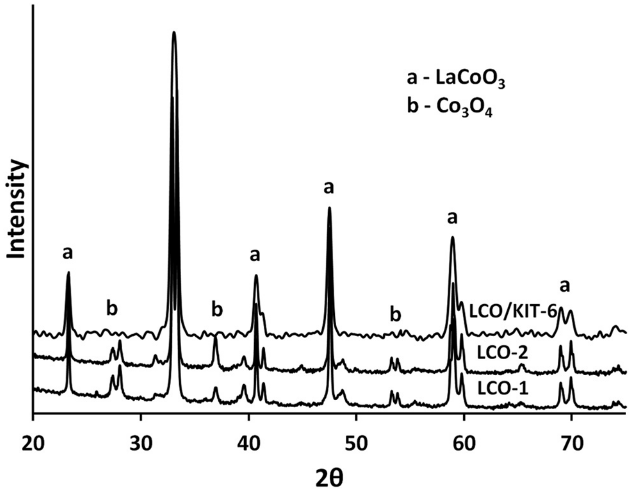

Figure 1: XRD of the synthesized samples after thermal treatment at 750°C.

synthesized is close to the ratio specified in the synthesis; the sodium content does not exceed 0.06% mass, which cannot significantly affect the catalytic behavior.

According to the XRD data (Figure 1), the obtained calcined samples are represented by the $LaCoO_3$ perovskite phase (JCDD PDF2 00-025-1060) with the inclusion of the Co_3O_4 phase (JCDD PDF2 00-009-0418) and a small admixture of the La_2O_3 phase (JCDD PDF2 00-005-0602).

Figure 2 shows the thermal curves of the initial LCO-1 precursor sample recorded in air. The thermogravimetric curve (TG) demonstrates the weight loss with increasing temperature up to 750°C, subsequently the weight remains constant, which indicates decomposition of all precursor phases and formation of the $LaCoO_3$ perovskite-type phase. A description of the observed thermal effects for the LCO-1 sample is given in Table 1.

Similar thermal curves were obtained for LCO-2. According to TA, the formation of LCO/KIT-6 sample is also completed at 700°C. Based on these results, the following heat treatment procedure was chosen: in air at 500°C for 3 h and at 750°C for 4 h.

In the thermal curves of sample reduction (Figure 3) in an argon + H_2 mixture flow, two effects with significant mass loss are observed in the temperature range 320–550°C, apparently indicating the destruction of the $LaCoO_3$ phase. Two exothermic effects are observed with maxima at 338 and 485°C, corresponding to step-by-step cobalt reduction: $Co^{3+} \rightarrow Co^{2+} \rightarrow Co^0$ [9,17]. Samples LCO-2 and LCO-KIT-6 have similar thermal curves. According to the TA data, the temperature of the beginning of cobalt reduction for the LCO/KIT-6 and CoAl reference samples are 480°C and 520°C, respectively. Therefore, for a uniform activation

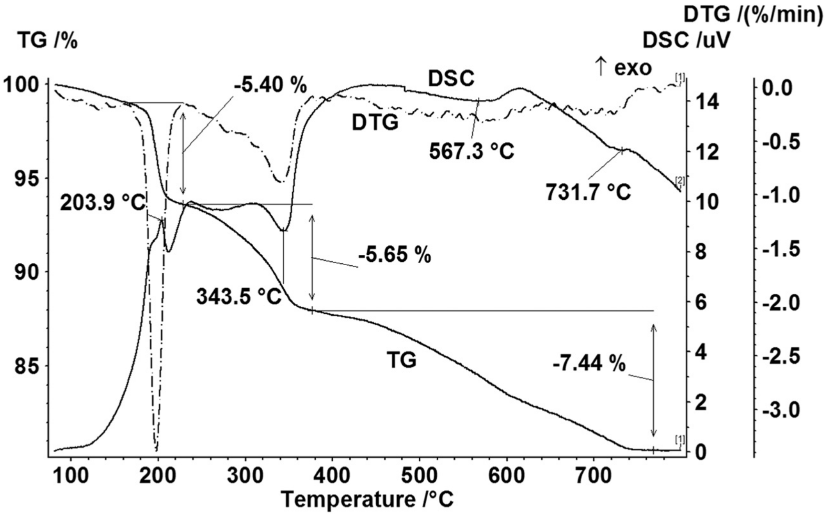

Figure 2: Thermal curves of the initial LCO-1 sample in air.

procedure, a reduction temperature of 520°C was chosen for all samples. The results of the catalytic tests of the synthesized samples are shown in Table 2.

According to the results of the catalytic tests, the presented LaCoO$_3$ samples have similar catalytic properties. At the same time, the catalytic properties of LaCoO$_3$ samples differ from those of CoAl catalyst, first in selectivity to alcohols. The effect of lanthanum-containing oxide support on the catalytic properties leading to a significant increase in the selectivity for alcohols can be seen. The catalytic properties of LCO-2 sample are distinctly different from those of the rest samples, characterized by a higher selectivity for light hydrocarbons. This may be due to the difference in the state of metallic cobalt particles in this sample. During its synthesis, in accordance with the published data, an excess of cobalt with respect to lanthanum was added, which led to the formation of an admixture of Co$_3$O$_4$ phase. Probably, the cobalt particles resulting from the reduction of this phase are not decorated by the lanthanum-containing oxide support, which leads to a decrease in the selectivity of the sample for alcohols with the predominant formation of uninteresting light hydrocarbons. The XRD data (Figure 4) of LCO-1 and LCO-2 samples after catalytic testing show the formation of a considerable amount of cobalt carbide, especially in LCO-2 sample. LCO/KIT-6 sample is amorphous after use. The formation of cobalt carbide may be due to the Co^0 particles not decorated by lanthanum oxide support. It is known that the formation of the La$_2$O$_2$CO$_3$ oxide layer on the surface is a characteristic of La-containing catalysts [16], which suggests that some parts of the Co^0 particles are decorated with

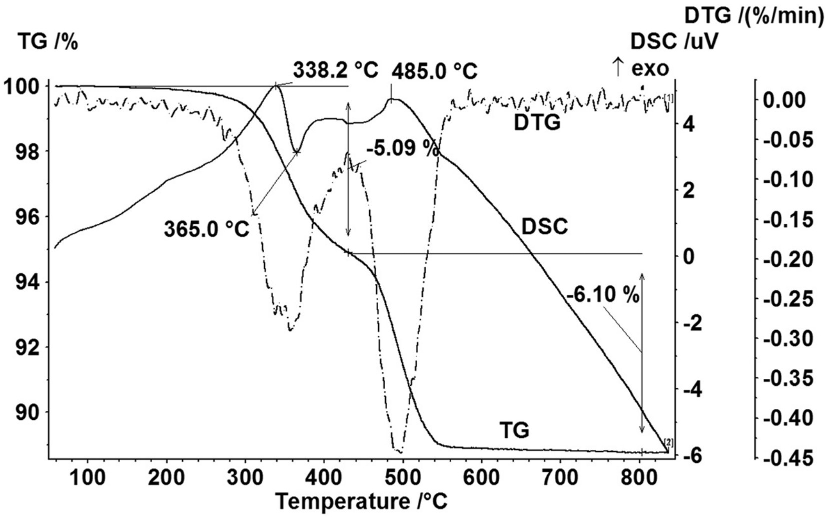

Figure 3: Thermal curves of LCO-1 sample in a mixture of argon + H$_2$.

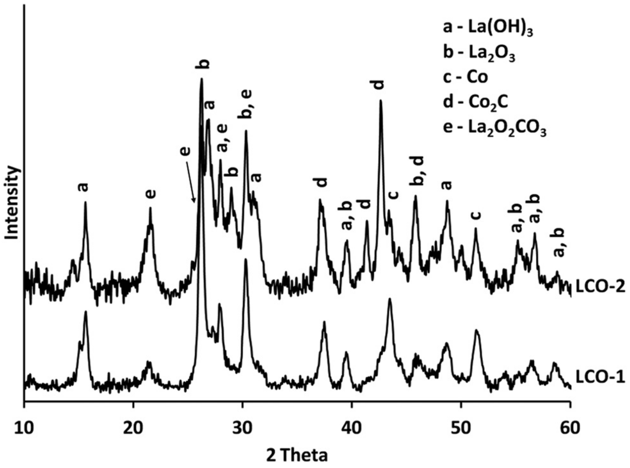

Figure 4: XRD of samples after catalytic tests.

lanthanum oxide. At the same time, the La-containing oxide support may activate CO_2 and suppress the Boudouard reaction ($2CO \leftrightarrow C + CO_2$), known to promote cobalt carbide formation [18]. The same $\alpha_{ASF,ROH}$ for the samples LCO-1 and LCO-2 indicates the absence of the effect of cobalt carbide on the shift in the distribution of alcohols, which does not confirm the proposed explanation in the literature [19,20].

The amount of hydrocarbons formed on LCO-1 and LCO/KIT-6, and, hence, the amount of water, is significantly less than that formed on the other two samples. Comparison of LCO-1 and LCO/KIT-6 reveals that the LCO/KIT-6, having increased specific surface area, is much more active. Despite a slight decrease in the overall selectivity to alcohols, a significant shift toward the formation of valuable higher alcohols is observed. This makes the process of converting syngas into alcohols very efficient on LCO/KIT-6, which looks promising for the production of motor fuels.

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Conflicts of interest: The authors declare no conflict of interest.

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