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INFLUENCE OF ORGANIC REDUCING AGENTS ON THE TEXTURAL AND CATALYTIC PROPERTIES OF $LaCoO_3$

Abstract. This work investigates the influence of soft organic templates on the structural, textural, and catalytic properties of perovskite-type $LaCoO_3$ catalysts synthesized by the co-precipitation method. D-glucose, D-fructose, and D-galactose were used as organic reducing agents. Precipitation was carried out using sodium hydroxide, after which the obtained precursors were subjected to successive thermal treatment in air at 300 and 750 °C. It was established that after calcination all samples predominantly form the $LaCoO_3$ perovskite phase with a minor admixture of Co_3O_4. According to nitrogen adsorption and electron microscopy data, the samples are characterized by a mesoporous structure with pore diameters in the range of 13–24 nm. Catalytic tests in the Fischer–Tropsch synthesis showed that the use of soft organic templates promotes an increase in alcohol yield and a decrease in methane and hydrocarbon formation. The highest catalytic efficiency in alcohol synthesis was demonstrated by the $LaCoO_3$-Gal and $LaCoO_3$-F samples.

Keywords: catalyst, perovskite, Fischer–Tropsch synthesis.

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Introduction. Catalysts based on perovskite-type complex oxides with the composition $LaCoO_3$ attract considerable interest due to their combination of high thermal stability, tunable redox properties, and the ability to form active metallic phases under catalytic reaction conditions. In particular, cobalt-containing perovskites are considered promising materials for syngas conversion processes, including Fischer–Tropsch synthesis and the production of oxygen-containing products such as alcohols [1,2]. One of the key factors determining the catalytic performance of perovskite materials is their textural properties, including specific surface area, porosity, and morphology. It is known that conventional synthesis methods for $LaCoO_3$ often lead to the formation of dense, low-porosity materials with low surface areas, which limits the accessibility of active sites. In this regard, the use of soft organic templates capable of influencing crystallization processes and pore structure formation during thermal treatment is of particular interest [3-6].

The application of organic compounds such as monosaccharides as soft templates and reducing agents makes it possible to control cation distribution in the precursor, as well as decomposition and phase formation processes during calcination. As a result, a perovskite structure with modified textural and morphological characteristics may be formed, which can significantly affect catalytic activity and selectivity [5,7-9].

The aim of this work is to study the influence of organic reducing agents – D-glucose, D-fructose, and D-galactose – on the textural, phase, and catalytic properties of $LaCoO_3$ catalysts prepared by the co-precipitation method, as well as to establish the relationship between their structural features and behavior in the Fischer–Tropsch synthesis reaction.

Materials and methods. Samples containing organic reducing agents were prepared using soft templates: D-glucose ($LaCoO_3$-Glu), D-fructose ($LaCoO_3$-F), and D-galactose ($LaCoO_3$-Gal). The catalysts were synthesized by the co-precipitation method using sodium hydroxide as the precipitating agent. The obtained precursors were subjected to successive thermal treatment in air at 300 °C for 3 h and 750°C for 4 h [2]. The thermal treatment program was selected based on thermogravimetric analysis, which showed that soft organic templates and their residues decompose at temperatures of about 360°C.

The specific surface area of all samples was determined by the Brunauer–Emmett–Teller (BET) method. Textural characteristics were investigated using nitrogen adsorption isotherms at 150°C on an ASAP-2400 instrument (Micromeritics, USA).

The phase composition of the samples was determined by X-ray diffraction (XRD) using a D-8 diffractometer (Bruker) with Cu Kα radiation. Measurements were carried out by stepwise scanning with an interval of 0.05° in the 2θ range of 20–80°.

Research results and discussion. According to XRD data, the obtained samples predominantly contain the $LaCoO_3$ perovskite phase (JCDD PDF2 00-025-1060) with a small amount of cobalt oxide Co_3O_4 (JCDD PDF2 00-009-0418). XRD patterns of samples calcined at 750°C are presented in Figure 1.

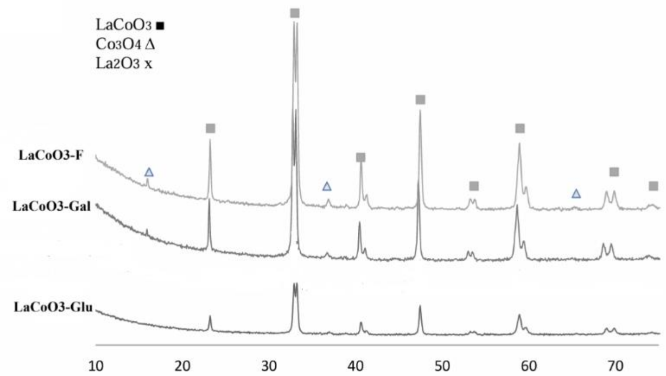

Fig. 1. XRD patterns of samples prepared using soft templates after calcination at 750°C

The pore diameter in samples based on monosaccharides is relatively small. This may be due to significant rearrangement of the crystal structure during perovskite formation as a result of disrupted cation homogenization during synthesis. The results of the investigation of the fine porous structure, clarifying the differences in the influence of the templates, are presented in Table 1.

Table 1

Summary of textural properties of the catalysts

Sample	S, m^2/g	D_{pores}, нм
$LaCoO_3$-Glu	6	24
$LaCoO_3$-Gal	6	13
$LaCoO_3$-F	6	17

According to TEM data (Fig. 2), the sample prepared using fructose consists of crystallized blocks of the target perovskite surrounded by an amorphous precursor phase containing lanthanum and cobalt oxides as well as a significant amount of carbon.

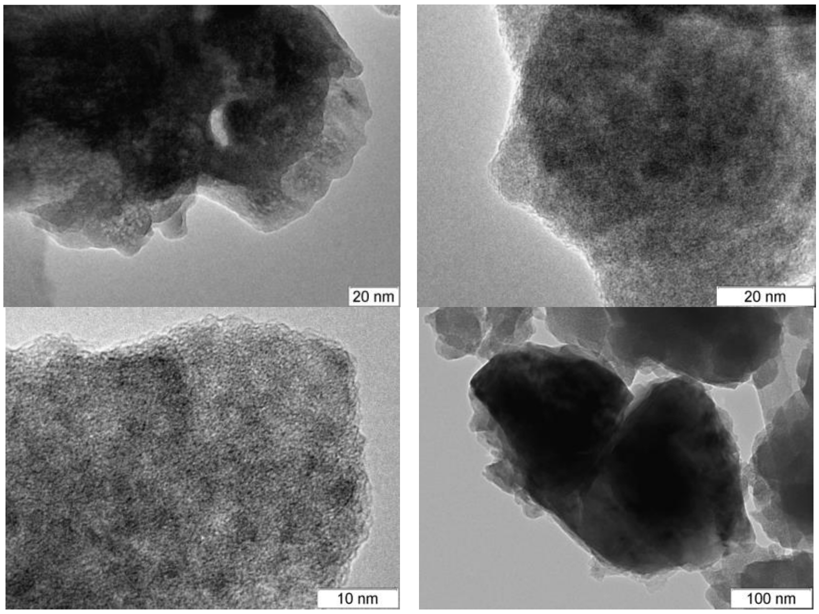

Fig. 2. TEM micrograph of the $LaCoO_3$-F sample

Table 2

Results of catalytic testing

Catalyst	C_2^+	CH_4	CO_2	R-OH	m_{cat}	X_{CO}	R-OH yield
$LaCoO_3$-Glu	9%	7%	1%	1%	2.0886	18.6%	14.8
$LaCoO_3$-Gal	10%	5%	6%	5%	2.0692	26.1%	58.1
$LaCoO_3$-F	6%	3%	4%	5%	2.0481	17.9%	51.7

The catalytic properties of all synthesized samples are similar. The highest CO conversion (26%) was observed on the $LaCoO_3$-Gal catalyst, while in the other two samples CO conversion was below 20%. Hydrocarbons and methane predominated in the gaseous products, whereas the amount of CO_2 was low and did not exceed 7% in all cases. The condensate consisted exclusively of alcohols. The use of soft organic templates allowed an increase in alcohol yield and a decrease in methane and hydrocarbon formation from 9–12% to 3–6%, respectively, as well as the elimination of CO_2 from the product composition. The application of soft templates slightly reduced methane and hydrocarbon yields; however, in the case of the $LaCoO_3$-Glu sample, the alcohol yield was noticeably lower. In the other two samples, the alcohol yield approached 60 mg/g.cat h^{-1}. Alcohols are the main liquid products of Fischer–Tropsch synthesis over reduced $LaCoO_3$ samples. The most active catalysts for alcohol synthesis are $LaCoO_3$-Gal, $LaCoO_3$-F, and bulk $LaCoO_3$, with alcohol productivities of at least 50 mg/g.cat · h^{-1}. During the reaction, all samples underwent irreversible structural degradation according to XRD data, resulting in the formation of complex phase mixtures. To determine the reasons for differences in product distributions, additional XRD analyses of the spent catalysts were carried out. Figure 3 shows the XRD patterns of samples based on soft templates after catalytic testing. In all samples, the presence of Co_3O_4 (formed due to oxidation of Co nanoparticles upon contact with air), La_2O_3, and $La(OH)_3$ phases was detected.

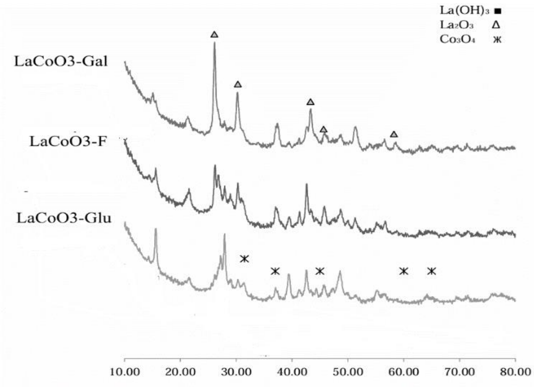

Fig. 3. XRD patterns of samples prepared using soft templates after reaction

Conclusion. It was established that the use of soft organic templates (D-glucose, D-fructose, and D-galactose) in the synthesis of $LaCoO_3$ catalysts by the co-precipitation method has a noticeable effect on their structural and textural characteristics. The application of organic templates contributes to an increase in alcohol yield and a reduction in methane and hydrocarbon formation. The highest catalytic efficiency in alcohol synthesis was demonstrated by the $LaCoO_3$-Gal and $LaCoO_3$-F samples.

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ОРГАНИКАЛЫҚ ТОТЫҚСЫЗДАНДЫРУШЫ АГЕНТТЕРДІҢ $LaCoO_3$ МАТЕРИАЛЫНЫҢ ТЕКСТУРАЛЫҚ ЖӘНЕ КАТАЛИТИКАЛЫҚ ҚАСИЕТТЕРІНЕ ӘСЕРІ

Аңдатпа. Бұл жұмыста бірге тұндыру әдісімен синтезделген перовскит типті $LaCoO_3$ катализаторларының құрылымдық, текстуралық және каталитикалық қасиеттеріне жұмсақ органикалық шаблондардың әсері зерттелді. Органикалық тотықсыздандырушы агенттер ретінде D-глюкоза, D-фруктоза және D-галактоза қолданылды. Тұндыру процесі натрий гидроксидін пайдалану арқылы жүргізіліп, алынған прекурсорлар кейін ауада 300 және 750 °C температураларда сатылы термиялық өңдеуден өткізілді. Күйдіруден кейін барлық үлгілерде негізінен $LaCoO_3$ перовскиттік фазасы түзілетіні және Co_3O_4 фазасының аз мөлшерде қоспа ретінде болатыны анықталды. Азот адсорбциясы мен электрондық микроскопия деректері бойынша үлгілер 13–24 нм аралығындағы кеуек диаметрімен сипатталатын мезокеуекті құрылымға ие. Фишер–Тропш синтезі реакциясындағы каталитикалық сынақтар жұмсақ органикалық шаблондарды қолдану спирттердің шығымын арттырып, метан мен көмірсутектердің түзілуін төмендететінін көрсетті. Спирттер синтезінде ең жоғары каталитикалық тиімділік $LaCoO_3$-Gal және $LaCoO_3$-F үлгілерінде байқалды.

Тірек сөздер: катализатор, перовскит, Фишер–Тропш синтезі.

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ВЛИЯНИЕ ОРГАНИЧЕСКИХ ВОССТАНАВЛИВАЮЩИХ АГЕНТОВ НА ТЕКСТУРНЫЕ И КАТАЛИТИЧЕСКИЕ СВОЙСТВА $LaCoO_3$

Аннотация. В данной работе исследовано влияние мягких органических шаблонов на структурные, текстурные и каталитические свойства перовскитных катализаторов $LaCoO_3$, синтезированных методом соосаждения. В качестве органических восстанавливающих агентов использованы D-глюкоза, D-фруктоза и D-галактоза. Осаждение проводили с использованием гидроксида натрия, после чего полученные прекурсоры подвергали последовательной термической обработке на воздухе при температурах 300 и 750 °C. Установлено, что после прокаливания во всех образцах преимущественно формируется перовскитная фаза $LaCoO_3$ с незначительной примесью Co_3O_4. Согласно данным адсорбции азота и электронной микроскопии, образцы характеризуются мезопористой структурой с диаметром пор в диапазоне 13–24 нм. Каталитические испытания в реакции синтеза Фишера–Тропша показали, что использование мягких органических шаблонов способствует увеличению выхода спиртов и снижению образования метана и углеводородов. Наивысшую каталитическую эффективность в синтезе спиртов продемонстрировали образцы $LaCoO_3$-Gal и $LaCoO_3$-F.

Ключевые слова: катализатор, перовскит, синтез Фишера–Тропша.