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G.D. Jetpisbayeva, B.K. Massalimova, A.B. Daulet

M.Kh. Dulaty Taraz State University, Taraz, Kazakhstan;

massalimova15@mail.ru**SYNTHESIS OF PEROFSKITE-LIKE
Co-CONTAINING CATALYST**

Abstract. There are several approaches to the preparation of catalysts with a developed surface based on oxides with a perovskite structure. Perovskites, due to the possibility of easy variation of chemical composition, make it possible to choose the optimal composition of the catalyst and surface area, and as a result it is possible to influence effectively the selectivity.

Perovskite-like LaMeO₃ oxides are one of the most promising catalysts for many oxidation processes due to their high activity in oxidative reactions and the stability in aggressive environment. Pekini method (polymer complexes method) and its simplified variant - citrate method are the most widely used for the synthesis of perovskite-like oxides.

This article reports about the synthesis of perovskite-like complex oxide LaCoO₃ obtained in two ways: hydrothermal, using ethylene glycol, and the citrate method using the template – mesoporous silica KIT-6. The structure of the samples obtained was determined by the XRD method. As a result, it was found that the catalysts have a perovskite structure.

Key words: LaCoO₃, perovskite, KIT-6.

Introduction. Cobalt catalysts are preferred for Fischer-Tropsch synthesis. The catalytic properties of cobalt catalysts are usually influenced by chemical interactions between the carriers and the metal, the texture of the catalysts and the morphology of crystals. Therefore, the balance of interactions between carriers and cobalt is very important [1-2]. It was previously shown that the type of precursor compound affects the physicochemical and catalytic properties of the reduced Co nanoparticles [3]. Such stable Co-containing compounds are mixed oxides with spinel, delafossite or perovskite structures.

Perovskites, due to the possibility of easy variation of the chemical composition, make it possible to choose the optimal composition of the catalyst and surface area, and as a result it is possible to influence effectively the selectivity for products. Perovskites have a flexible structure and are able to undergo significant changes with a possible decrease in symmetry or the formation of defects, while remaining within the framework of a perovskite structural type. There are several approaches to the preparation of catalysts with a developed surface based on oxides with a perovskite structure.

Perovskite-like LaMeO₃ oxides are one of the most promising catalysts for many oxidation processes due to their high activity in oxidative reactions and the stability in aggressive environment. Pekini method (polymer complexes method) and its simplified variant - citrate method are the most widely used for the synthesis of perovskite-like oxides [4]. The method of polymer complexes is a method for the synthesis of highly homogeneous and highly dispersed material oxides by using a complexing agent and the intermediate production of a polymer gel. Citric acid is usually used as the complexing agent, and ethylene glycol as the copolymer. However, the method of polymer complexes has its drawbacks, since the cations of some metals, for example, silver and platinum can't stabilize in the resulting compound: they can be easily reduced by an organic complexing agent. Another possible way to obtain perovskite-like oxides is the hydrothermal method and template synthesis, which is the introduction of a template with a developed surface at the stage of deep interaction of the components [5].

This article reports the synthesis of perovskite-like complex oxide LaCoO_3 obtained in two ways: hydrothermal, using ethylene glycol, and the citrate method using the template — mesoporous silica KIT-6. The proposed methods for the synthesis of catalysts ensure the homogenization of cations in the synthesized precursor compound and the homophasis of the compound obtained.

The structure of the samples obtained was determined by the XRD method. As a result, it was found that the catalysts have a perovskite structure. As a result, it was found that the catalysts have a perovskite structure.

Materials and methods. The following reagents were used in the work: $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (хч, Реахим, ТУ 6-09-4676-83), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (ч, Реахим, ГОСТ 4528-78), NaOH (хч, Экрос, ГОСТ 4328-77), HNO_3 (осч, ГОСТ-11125-84), ethylene glycol (хч, Реахим, ГОСТ 19710-83), citric acid (чда, Экрос, ГОСТ 36-52-69), $\text{C}_2\text{H}_5\text{OH}$ (Реахим, ГОСТ Р 51999-2002), HCl (Гранхим, ГОСТ 3118-77), butanol-1 (Реахим, ГОСТ 6006-78), Pluronic P123 (Aldrich, MW 5800 O20P070E020), ethanol (ГОСТ Р 51999-2002), tetraethoxysilane (TEOS) (Компонент реактив, СТП ТУ КОМП 2-312-11) For the preparation of solutions, distilled water was used.

Two samples of LaCoO_3 with different ratios La:Co were obtained by the hydrothermal method [6] in the presence of ethylene glycol. The first sample of LaCoO_3 (LCO-1) was obtained by solvation of 0.06 mol of lanthanum nitrate and 0.06 mol of cobalt nitrate in 80 ml of water. Then 0.16 mol of ethylene glycol was added to the salt solution.

Separately, 120 ml of a 4M sodium hydroxide solution was prepared in a polypropylene beaker. Then, salt solution with a soft template was added drop wise to the sodium hydroxide solution. The pH of the solution changed from 3.0 to 13 with the formation of a thick purple precipitate of a mixture of cobalt alcoholates and lanthanum hydroxide. Then, nitric acid was added drop wise to the solution until $\text{pH} = 10$, the resulting suspension was stirred for 2 hours. Next, a propylene beaker with a suspension was closed tightly with a lid and placed in a heating oven for 24 hours at a temperature of 100°C . Slow oxidation of templates by NO_3^- anions which are present in the solution occurs at 100°C followed by the release of nitrogen or nitrous oxide. Formation of a mixture of carboxylic acids undergoing further degradation with the gradual separation of terminal carboxyl groups is observed in this process (figure 1).

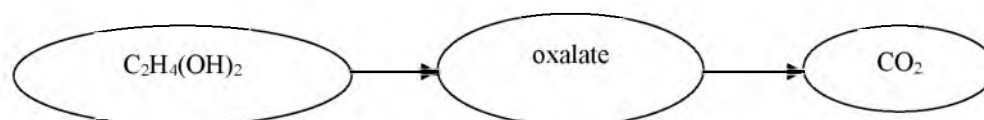


Figure 1 - The scheme of the oxidation of ethylene glycol in hydrothermal conditions

A slow decrease of pH is observed due to the isolation of oxidation products, which leads to an increase in the concentration of cobalt and lanthanum cations in the solution. At the end of the synthesis, the brown suspension was washed with 5 L of distilled water on a filter and dried under an infrared lamp. The obtained powder was calcined in air at 500°C for 3 hours and 750°C for 4 hours. The second sample LCO-2 was obtained in a similar way, the amount of metal cations in this synthesis was 0.06 mol of lanthanum nitrate and 0.08 mol of cobalt nitrate. This ratio was chosen due to the fact that part of cobalt is lost due to its better solubility in comparison with lanthanum [6].

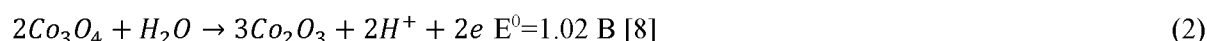
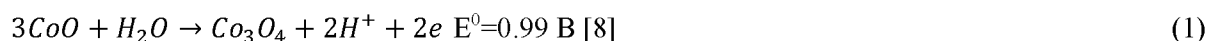
According to published data [7], the mesoporous silicon carrier KIT-6 has a developed specific surface. On the one hand, its use in the synthesis of LaCoO_3 by the citrate method can significantly increase the surface of the forming perovskite. On the other hand, the use of citric acid and, as a consequence, the creation of an acidic environment under synthesis conditions prevents the chemical participation of SiO_2 in the formation of the sample.

The synthesis of the mesoporous silicon carrier KIT-6 was performed according to the procedure [7]. The following ratios of $\text{TEOS} / \text{P123} / \text{HCl} / \text{H}_2\text{O} / \text{Butanol} = 1 \text{ mol} / 0.017 \text{ mol} / 1.83 \text{ mol} / 1.95 \text{ mol} / 1.31 \text{ mol}$ were used to calculate the weights. The synthesis procedure is as follows: 9 g of P123 and 17.40 g of HCl (35%) were dissolved in 325 g of water, mixed until the solution was completely homogenized. Next, 9 g of butanol was added and stirred at 35°C for 1 hour. Then, 19.35 g of TEOS was added. In this case, significant heat release was observed. The resulting solution was stirred at 35°C for 24 hours. In the last step, the mixture was hydrothermally treated at 100°C for 24 hours. Next, the resulting precipitate was filtered, washed with alcohol and dried under an infrared lamp. The obtained precursor was subjected

to heat treatment for 4 hours at 500 ° C, during which the organic components of the precursor were removed and the desired template KIT-6 was formed.

A sample of LaCoO₃/KIT-6 (LCO / KIT-6) was obtained by the citrate method. Samples of salts of (Co(NO₃)₃ × 6H₂O (0.02 mol) 5.83 g and La(NO₃)₃ × 6H₂O (0.02 mol) 8.67 g and citric acid were dissolved in 60 ml of ethanol. 6 g KIT-6 was mixed with 60 ml of water and allowed to mix for 30 minutes. Then, a solution of salts was added dropwise into the resulting suspension. The resulting mixture was kept for 24 hours with continuous stirring at 35 °C, and then, evaporated in a rotary evaporator at 95 °C to form a gel, which was dried under an infrared lamp, grinded into powder and calcined at 500 °C for 3 hours and at 700 °C - 4 hours. Then, a sample with KIT-6 was kept in 500 ml of a 7% NaOH solution at 70 °C for 15 minutes, filtered and washed on a filter with 2 L of distilled water at a temperature of 75 °C four times, then dried under an infrared lamp.

In the synthesis by the citrate method, an excess of citric acid over the NO₃⁻ anions, calculated on the conversion of the latter into nitrogen, provides an amorphous gel [4], from which a single-phase LaCoO₃ oxide was formed during heat treatment. The resulting powder contains in its structure lanthanum and cobalt as part of complex chelate complexes that decompose in stages during heat treatment at 1800C and 3500C with the release of water vapor, NO₂ and CO₂. At the limiting stage, cobalt is oxidized with air oxygen at 7000 ° C and a perovskite structure is formed:



The phase composition of the samples was determined by X-ray phase analysis (XRD) on a D-8 diffractometer (Bruker) using Cu-Kα radiation by point-to-point scanning method with an interval of 0.050 in the angle range 2θ from 20 ° to 80 °.

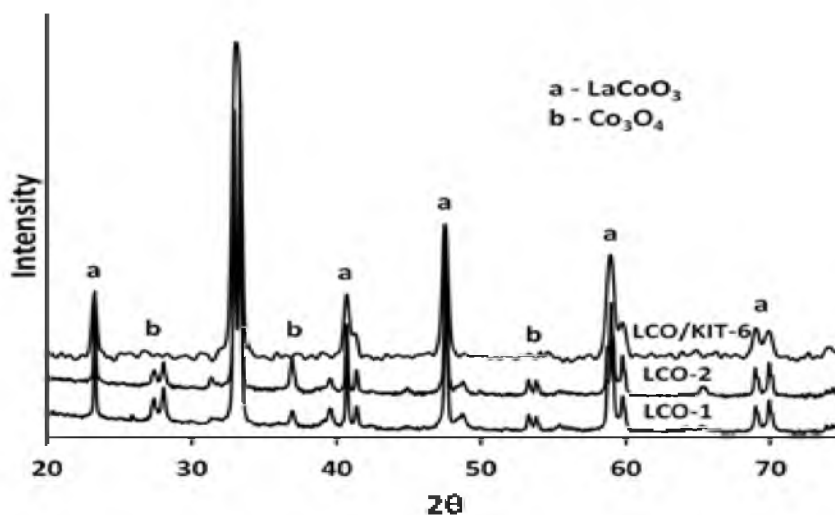


Рисунок 2 - Данные рентгенофазового анализа синтезированных образцов

According to the XRD data (Fig. 2), the samples obtained are represented by the LaCoO₃ perovskite phase (JCDD PDF2 00-025-1060) with the inclusion of the Co₃O₄ phase (JCDD PDF2 00-009-0418) and a small admixture of the La₂O₃ phase (JCDDPDF2 00-022-0641).

The results of the XRD analysis show that the samples obtained are represented by the perovskite phase. The resulting catalysts with perovskite structure are of great interest for the Fischer-Tropsch synthesis. Perovskites, due to the possibility of easy variation of the chemical composition, allow to choose the optimal composition and surface of the catalyst, as a result it is possible to influence effectively the selectivity. In this regard, further study the obtained Co-containing catalysts with the perovskite

structure by other physicochemical methods is planned and the possibility of using them for Fischer-Tropsch synthesis is considered.

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Со-ҚҰРАМДЫ ПЕРОВСКИТ ҚҰРЫЛЫМДЫ LaCoO_3 КАТАЛИЗАТОРЫН СИНТЕЗДЕУ

Анотация. Перовскит құрылымы бар оксидтерге негізделген, беттік ауданы үлкен катализаторларды дайындаудың бірнеше тәсілдері бар. Перовскиттер, химиялық құрамының икемді өзгеруінің мүмкіндігіне байланысты катализатордың құрамын және оның беттік ауданын оңтайлы таңдауға мүмкіндік береді, нәтижесінде өнімнің селективтілігіне әсер етуі мүмкін.

Перовскит құрылымды оксидтер LaMeO_3 тотығу реакцияларындағы белсенділігі мен агрессивті ортаға тұрақтылығына байланысты көптеген тотығу процестерінің перспективті катализаторларының бірі болып табылады. Перовскит құрылымды оксидтерді синтездеу үшін Пекини әдісі (полимерлі кешендер әдісі) және оның жеңілдетілген нұсқасы цитратты әдіс кеңінен қолданылады. Бұл мақалада LaCoO_3 перовскит құрылымды күрделі оксид екі жолмен синтезделді: этиленгликоль қолдана отырып, гидротермалды әдіспен және қатты темплат мезопорлы кремнезем КІТ-6 қатысында, цитрат әдісі. Алынған үлгілердің құрылымы РФА әдісімен анықталды. Нәтижесінде катализаторлардың перовскиттік құрылымға ие екендігі анықталды.

РФА мәліметтеріне сәйкес алынған үлгілердің фазалық құрамы LaCoO_3 перовскиттік фазасына (JCDD PDF2 00-025-1060) сай келеді. Құрамында аз мөлшерде Co_3O_4 фазасының (JCDD PDF2 00-009-0418) және La_2O_3 фазасының (JCDDPDF2 00-022-0641) елемуге болатын қоспалары бар.

РФА талдау нәтижелері алынған үлгілердің құрылымында перовскиттік фаза түзілгендігін көрсетеді. Перовскиттік құрылымға ие Со-құрамды катализаторлар Фишер-Тропш синтезінде қолдануға үлкен қызығушылық тудырады. Себебі, перовскиттердің, химиялық құрамының икемді өзгеру мүмкіндігіне байланысты, олар катализатордың оңтайлы құрамы мен беттік ауданын ұлғайтуға мүмкіндік береді, нәтижесінде селективтілікке тиімді әсер етуі мүмкін. Осыған байланысты алынған перовскиттік құрылымы бар Со құрамды катализаторларды болашақта басқа физика-химиялық әдістермен зерттеу және Фишер-Тропш синтезінде қолдану мүмкіндігі қарастырылады.

Түйін сөздер: LaCoO_3 , перовскит, КІТ-6

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СИНТЕЗ ПЕРОВСКИТОПОДОБНОГО Со-СОДЕРЖАЩЕГО КАТАЛИЗАТОРА

Анотация. Существует несколько подходов к получению катализаторов с развитой поверхностью на основе оксидов со структурой перовскита. Перовскиты, благодаря возможности гибкого варьирования химического состава позволяет подобрать оптимальный состав катализатора и поверхности, вследствие чего возможно эффективно влиять на селективность по продуктам.

Перовскитоподобные оксиды LaMeO_3 являются одними из наиболее перспективных катализаторов для многих процессов окисления, благодаря своей высокой активности в окислительных реакциях и стабильности агрессивной среде. Для синтеза перовскитоподобных оксидов наибольшее распространение получил метод Пекини (метод полимерных комплексов) и его упрощенный вариант – цитратный метод. В этой статье было синтезировано перовскитоподобный сложный оксид LaCoO_3 двумя способами: гидротермальным, с применением этиленгликоля, и цитратным способом с внесением темплата – мезопористого кремнезема КІТ-6. Структуры полученных образцов было определено РФА методом. В результате было установлено, что катализаторы имеют перовскитную структуру.

Согласно данным РФА полученные образцы представлены фазой перовскита LaCoO_3 (JCDD PDF2 00-025-1060) с включением фазы Co_3O_4 (JCDD PDF2 00-009-0418) и небольшой примесью фазы La_2O_3 (JCDDPDF2 00-022-0641).

Результаты РФА анализа показывают, что полученные образцы представлены фазой перовскита. Полученные катализаторы со структурой перовскита представляют большой интерес в синтезе Фишера-Тропша. Так как, перовскиты, благодаря возможности гибкого варьирования химического состава позволяет подобрать оптимальный состав и поверхности катализатора, вследствие чего возможно эффективно влиять на селективность. В связи с этим полученные Со-содержащие катализаторы со структурой перовскита в будущем планируется исследовать другими физико-химическими методами и рассмотреть возможность использования в синтезе Фишера-Тропша.

Ключевые слова: LaCoO₃, перовскит, KIT-6.

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