N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.34**
Volume 2, Number 440 (2020), 138 – 144

UDC 54.057:661.722

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SYNTHESIS AND STUDY OF STRUCTURAL PROPERTIES OF COMPOSITES BASED ON NI-RU FOR STEAM CONVERSION OF ETHANOL

Abstract. Catalyst precursors, substituted by rare-earth and transition metals, promoted with Ru nanoparticles using the modified Pechinimethod (Organic polymeric precursor) have been synthesized. To transform biofuel (ethanol) into hydrogen from the obtained active phases, three different methods were used to synthesize composites with the general formula [$LaMn1\text{-}xBxO_3 + \delta$ / $Ln_{1\text{-}y}Zr_yO_2$] (1: 1 by mass), B = Ni, Ru, Ln = Pr, Sm , Ce. Structural and surface properties of the obtained samples of complex oxides and composites were studied using the BET and XPA methods. The textural and structural characteristics of composites differing in the methods of their preparationare presented.
Key words: perovskite, fluorite, composites, biomass, hydrogen.

Introduction

Fossil fuels are widely used, but their resources are limited. Therefore, the development of new fuels is necessary, and currently much attention is paid to renewable energy sources [1]. Biomass as a renewable raw material is not only the subject of numerous scientific studies, but in some countries it largely replaces traditional fossil energy sources. To date, one of the most promising methods for transforming biomass into fuel and energy is catalytic steam conversion of the liquid products of biomass processing into hydrogen and synthesis gas [2].

In this regard, the need to create new catalysts for the steam conversion of ethanol to hydrogen and synthesis gas is of great interest. Well known catalysts for steam reforming of oxygen-containing compounds are usually noble [3-5] or transition metals [6-9] deposited on the surface of porous supports. The main problem that impedes their industrial application is the coke formation on the surface of catalysts and, as a consequence, their deactivation [6-10].

Nanocrystalline oxides with the structure of fluorite, perovskite and spinel and their nanocomposites containing cations of rare-earth and transition metals, capable of changing their oxidation state, have high mobility and reactivity of oxygen. Such oxides are one of the most promising carriers resistant to coke formation for catalysts for the conversion of hydrocarbons or oxygen-containing compounds into synthesis gas [11,12].

There are several approaches to the preparation of oxide nanocomposites with the structure of perovskite and fluorite. The method of synthesis of nanocomposite materials should provide high chemical uniformity of the obtained complex oxides along with their high dispersion. Among many methods for preparing catalysts, the high spatial uniformity of the distribution of cations in mixed oxides is ensured by the method of the so-called ester polymer precursors (Pechini method) with the addition of chelating agents such as citric acid, ethylene diamine (ED) and ethylene glycol [13].

Based on this, the aim of this work is to synthesize and study the texture properties of Ni-Ru-based composites intended for ethanol steam reforming.

Experimental part

Preparation of active ingredients

To prepare the samples $Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$ and $LaMn_{0.45}Ni_{0.4}5Ru_{0.1}$ according to the Pechinimethod, we used crystalline hydratesPr $(NO_3)_3{\cdot}6H_2O$(pur.), Sm $(NO_3)_2{\cdot}6H_2O$ (puriss), Ce $(NO_3)_2 \cdot 6H_2O$ (p.a.), $ZrOCl_2$ (puriss),La $(NO_3)_3{\cdot}6H_2O$ (puriss), $Ni(NO_3)_3{\cdot}6H_2O$ (p.a.),$RuOCl_3$ (p.a.), $Mn(NO_3)_2 \cdot 6H_2O$ (puriss), citric acid (LA, puriss), ethylene glycol (EG, p.a.), ethylenediamine (ED, pur).

The exact molar masses of nitrates were determined by thermal analysis. Ethylene glycol and citric acid were used as complexing agents. Ethylene diamine is added to further polymerization of the system. Reagents were taken in molar ratios of LC: EG: EDA: Σν (metals) = 3.75: 11.25: 3.75: 1. Citric acid was dissolved in ethylene glycol with vigorous stirring and gentle heating (60-80 ° C). Crystalline hydrates of metal nitrates were added to the resulting solution cooled to room temperature with vigorous stirring, then ethylenediamine was added dropwise. Full homogenization was expected in 2 h. The resulting mixture was evaporated with stirring to obtain a viscous polymer, calcined in a muffle furnace at 700 ° C during 5 hours.

Synthesis of Nanocomposites

Nanocomposites based on $Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$ $LaMn_{0.45}Ni_{0.4}Ru_{0.1}$complex oxides at a 1: 1 ratio were synthesized using a modified Pechini polymeric precursor method, followed by calcination with 700°C for 4 hours.

Physico-chemical studies of the samples obtained

The phase composition of the samples was determined by x-ray phase analysis (XRD). Diffraction patterns were obtained using a Bruker Advance D8 diffractometer with CuKα radiation. Scanning was carried out in the angle range of 20-80 (2Θ) with a scan step of 0.05 (2Θ). Identification of the phases obtained and quantitative calculations were obtained using the ICDD X-ray file cabinet.

The specific surface area of the synthesized samples was measured by the express version of the BET method for thermal desorption of argon on a SORBI-M device.

Results and discussion

Using the method of low-temperature nitrogen adsorption, the specific surface area of the obtained oxides and nanocomposites was calculated.

Table 1 -Textural properties of complex oxides and synthesized composites

№	Composition of Composites	Method of preparation	Calcination,°C	Surface, m^2/g	Bulkdensity, kg/m^3
1	$Pr_{0.15}$ $Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$	Pechini	700	75	-
2	$LaMn_{0.45}Ni_{0.45}$ $Ru_{0.1}O_3$	Pechini	700	8	-
3	$Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$ и $LaMn_{0.45}Ni_{0.45}Ru_{0.1}O_3$	Polymer	700	36	1,3621
4	$Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$ и $LaMn_{0.45}Ni_{0.45}Ru_{0.1}$ O_3	one-pot synthesis	700	49	1,4691
5	$Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$ и $LaMn_{0.45}Ni_{0.45}Ru_{0.1}O_3$	Ultrasonic dispersion	700	61	1,1174

From the results presented in table 1, it is seen that the fluorite-like complex oxide with the composition $Pr_{0.15}$ $Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$prepared by thePechinimethod has the largest specific area - 75 m2/g. The composite prepared by the method of ultrasonic dispersion is distinguished by a high specific surface as well. The composites prepared by the Polymer and One-pot synthesis methods showed 36 and 49 m^2/g, respectively. The lowest specific surface index has a perovskite-like complex oxide with the composition $LaMn_{0.45}Ni_{0.45}Ru_{0.1}O_3$prepared by the Pechinimethod. It is known thatperovskites generally have a low specific surface area [14, 15].

The phase composition of the sample of complex oxide $Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$prepared by the Pechini method and calcinedat 700 ° C in the angle range 2θ, 20-80 ° C is shown in figure 1.

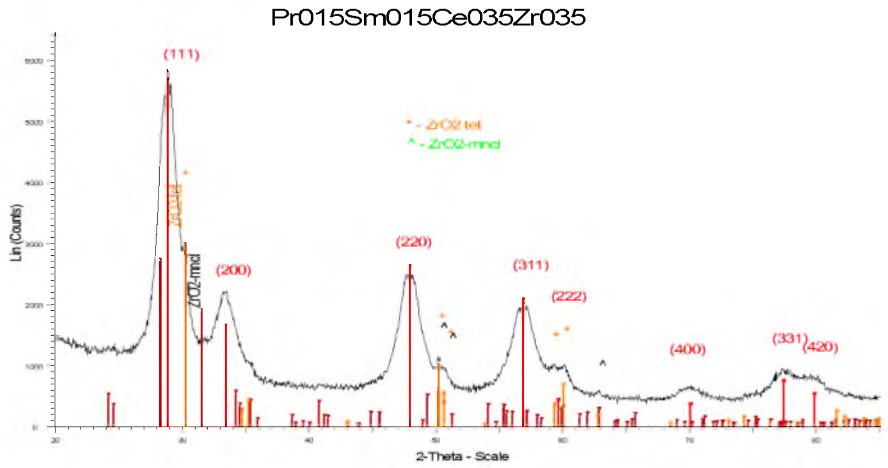

Figure 1 - Diffraction pattern of the $Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$sample

According to X-ray diffraction data (figure 1), a sample of the complex oxide $Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$ is a single-phase well crystallized system, which is a solid fluorite-like solution of cubic type PrSmCeZrO (Fm3m) with a small admixture of phases of monoclinic and tetragonal zirconium oxides.

Using the XRD method, the phase composition of the complex oxide sample $LaMn_{0.45}Ni_{0.45}Ru_{0.1}O_3$prepared by the Pechini method, calcined at 700 ° C in the angle range 2θ, 20-80 ° C (figure 2) was determined.

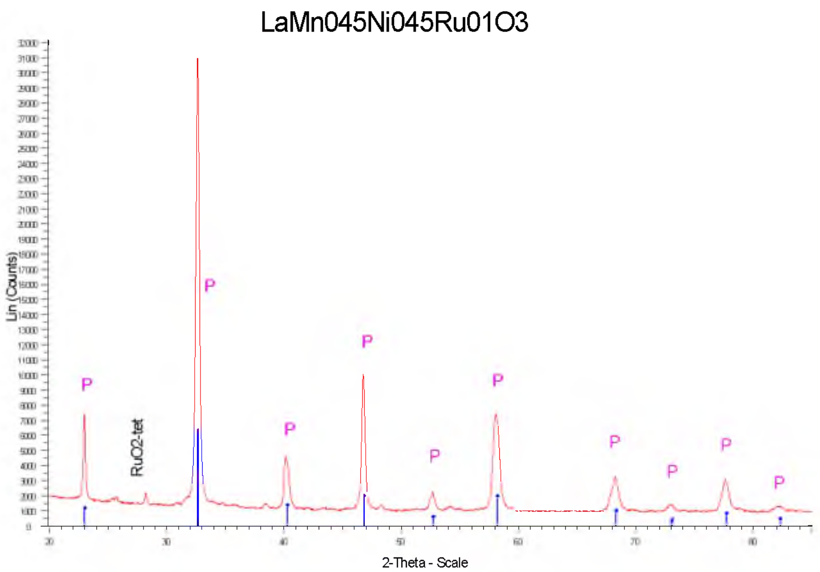

Figure 2 - Diffraction pattern of the $LaMn_{0.45}Ni_{0.4}Ru_{0.1}O_3$sample

According to the XRD data (figure 2), the phase composition of the LaMnNiRuOnanocomposite is crystallized in the structural type of perovskite with orthorhombic symmetry.

Next, the phase compositions of composites synthesized by the Polymer and One-pot synthesis methods and the ultra dispersion method (figure 3) based on complex oxide precursors were determined.

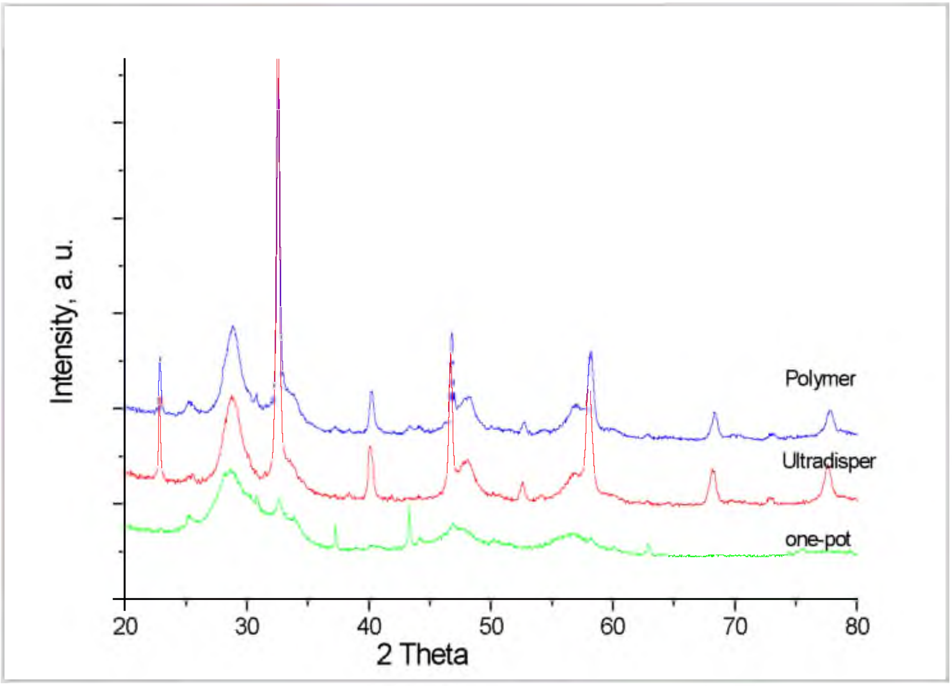

Figure 3 - X-ray diffraction patterns of composites

From the data presented (figure 3) it can be seen that upon application of various active components, such as Ni, Mn, Ru, the fluorite-like structure of composites obtained using the Polymer and ultradispersion methods is preserved. Whereas in a composite synthesized by the One-pot method, the fluorite-like structure is deformed. The crystalline phase — NiO was identified in composite, obtained using the Polymer method.

Surface promotion of the support by rare-earth elements inhibits the growth of nickel crystallites, preventing the formation of large particles necessary for the formation of coke, and also complicates the reoxidation of metallic nickel during the reaction [16,17,18,19]

Complex oxides with a perovskite structure in addition to high oxygen mobility have a number of additional unique properties. Due to this, they are sometimes called "replacement of noble metals" in the application to catalysis [20]. Catalysts based on substituted precursors for the ethanol steam reforming process based on perovskites $LaFeNiO_3$ [21], $La_{1-x}AxFe_{1-y}NiyO_3$ (A = Ca, Sr) [22.23], $La1\text{-}xSrxFe_{1-y}Co_yO_3$ [24], $La_{1-x}CaxFe_{1-x}Co_xO_3$ [25] and $LaXCoO_3$ (X = Mg, Ca, Sr, Ce) [26] are well known.

The results of this work are of particular interest in the field of modern catalysis in obtaining renewable energy sources, and also require further research. The data obtained contribute to the solution of the development of domestic catalyst production

Conclusions

This study presents the results of the synthesis of single-phase nanocrystalline complex oxides with the general formula [LaMn1-xBxO3 + δ / Ln1-yZryO2] (1: 1 by mass), B = Ni, Ru, Ln = Pr, Sm, Ce, with fluorite (doped cerium-zirconium oxide) and perovskite structures by thePechinimethod.

Synthesis methods are proposed that lead to the formation of a complex perovskite-fluorite system with cations uniformly distributed in one structure and a developed interphase phase. The influence of the synthesis method on the structural properties of the oxide system is shown. The results of the study showed that in the synthesis of composite structures, the most effective is the method of ultrasonic dispersion.

Acknowledgments

This work was financially supported by M.Kh. DulatiTaraz State University, Taraz, Kazakhstan. Research work was carried out in the scientific laboratory of "Chemistry and Chemical Technology"

department of TarSU and "Deep Oxidation Catalysts" laboratory of G.K. Boresky institute of catalysis SB RAS, Novosibirsk, Russia.

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ЭТАНОЛДЫҢ БУ АЙНАЛЫМЫ ҮШІН NI-RU НЕГІЗІНДЕГІ КОМПОЗИТТЕРДІ СИНТЕЗДЕУ ЖӘНЕ ОЛАРДЫҢ ҚҰРЫЛЫМДЫҚ ҚАСИЕТТЕРІН ЗЕРТТЕУ

Аннотация. Қазба отындары кеңінен қолданылады, бірақ олардың ресурстары шектеулі. Сондықтан отынның жаңа түрлерін жасау қажет. Қазіргі уақытта жаңартылатын энергия көздеріне көп көңіл бөлінуде. Биомасса- шикізат ретінде көптеген ғылыми зерттеулердің тақырыбы гана емес, сонымен қатар, кейбір елдерде дәстүрлі қазба энергия көздерін алмастыруда. Бүгінгі таңда биомассаны отын мен энергияға айналдырудың перспективті әдістерінің бірі – биоотынды сутегі мен синтез газына булы каталитикалық айналдыру болып табылады.

Осыған байланысты этанолды сутегі мен синтез газына бу айналымына қажетті жаңа катализаторларды жасау қажеттілігі үлкен қызығушылықты тудырды. Құрамында оттегі бар қосылыстардың булы айналымының катализаторлары әдетте кеуекті тасымалдағыштарға қондырылған асыл немесе ауыспалы металдар болып табылады. Оларды өнеркәсінте қолдануға кедергі келтіретін негізгі мәселе, катализаторлардың көмірленуі және соның салдарынан олардың жарамсыздығы болып табылады.

Құрамында сирек кездесетін және ауыспалы металдардың катиондары бар флюорит, перовскит және шпинель құрылымды нанокристалды оксидтер мен олардың нанокомпозиттері тотығу күйін өзгертуге қабілетті және оттегінің жогары қозгалгыштыгы мен реакцияласу қабілетіне ие. Мұндай оксидтер көмірсутектерді немесе оттегі бар қосылыстарды синтез газы мен сутегіне айналдыруға қажетті катализаторлардың көмірленуіне тұрақты тиімді катализаторлардың бірі болып табылады.

Осыган сәйкес, бұл жұмыстың мақсаты - этанолдың бу айналымындагы Ni-Ru негізіндегі композиттерді синтездеу және олардың құрылымдық қасиеттерін зерттеу болып табылады.

Ru нанобөлшектерімен промоторланган, сирек кездесетін және ауыспалы металдармен алмастырылған катализаторлардың прекурсорларының синтезі, полимерлі органикалық прекурсорлардың модифицирленген әдісімен (Пекини) жүргізілді. Биоотыннан (этанол) сутегі алу үшін, алынган белсенді фазалардан үш түрлі әдіспен жалпы формуласы $[LaMn_{1-x}B_xO_{3+\delta}/Ln_{1-y}Zr_yO_2]$ (1:1 масса бойынша), B = Ni, Ru, Ln = Pr, Sm, Ce композиттер синтезделді.Синтездеу әдістерінің үлгілердің құрылымдық және беттік қасиеттеріне әсерін рентгендік фазалықжәне BET әдістерімен зерттелді.Синтездеу әдістерінің ерекшелігіне байланысты композиттердіңқұрылымдық және беттік қасиеттері сипатталды.

Бұл жұмыстың нәтижелері заманауи катализ саласында жаңартылатын энергия көздерін алуда ерекше қызығушылық тудырады, осыган орай, одан әрі зерттеуді қажет етеді. Алынган мәліметтер катализаторлардың отандық өндірісін дамыту мәселелерін шешуге ықпал етеді.

Түйін сөздер: перовскит, флюорит, нанокомпозиттер, биомасса, сутегі.

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СИНТЕЗ И ИЗУЧЕНИЕ СТРУКТУРНЫХ СВОЙСТВ КОМПОЗИТОВ НА ОСНОВЕ NI-RU ДЛЯ ПАРОВОЙ КОНВЕРСИИ ЭТАНОЛА

Аннотация. Ископаемые виды топлива широко используются, однако их ресурсы ограничены. Поэтому разработка новых видов топлива необходима, и в настоящее время большое внимание уделяется возобновляемым источникам энергии. Биомасса как возобновляемое сырье не только является предметом

многочисленных научных исследований, но в некоторых странах в значительной мере заменяет традиционные ископаемые источники энергии. На сегодняшний день одним из самых перспективных методов трансформации биомассы в топливо и энергию является каталитическая паровая конверсия жидких продуктов переработки биомассы в водород и синтез-газ.

В этой связи необходимость создания новых катализаторов для паровой конверсии этанола в водород и синтез-газ вызывает большой интерес. Известные катализаторыдля паровой конверсии кислородсодержащих соединений обычно представляют собой благородные или переходные металлы, нанесенные на поверхностьпористых носителей. Основной проблемой, затрудняющей их промышленное применение, является зауглероживание катализаторов икак следствие - их дезактивация.

Нанокристаллические оксиды со структурой флюорита, перовскита и шпинели и их нанокомпозиты, содержащие катионы редкоземельных и переходных металлов, способные изменять свою степень окисления, обладают высокой подвижностью и реакционной способностью кислорода. Такие оксиды являются одними из наиболее перспективных носителей, устойчивых к зауглероживанию катализаторов, для превращения углеводородов или кислородсодержащих соединений в синтез-газ и в водород.

Исходя из этого,цельюданной работы является синтез и изучение текстурных свойств композитов на основе Ni-Ru, предназначенных для паровой конверсии этанола.

Синтезированы предшественники катализаторов, замещенные редкоземельными и переходными металлами промотированных наночастицами Ru с помощью модифицированного метода organic polymeric precursor (метод Пекини). Для трансформации биотоплива (этанола) в водород, из полученных активных фаз тремя разными методами синтезированы композиты с общей формулой [$LaMn_{1-x}B_xO_{3+\delta}/Ln_{1-y}Zr_yO_2$] (1:1 по массе), B = Ni, Ru, Ln = Pr, Sm, Ce.. Структуные и поверхностные свойства полученных образцов сложных оксидов и композитов изучены с помощью методов БЭТ и РФА. Представлены текстурные и структурные характеристики композитов, отличающиеся в зависимости от методов его приготовления.

Результаты настоящей работыпредставляют особый интерес в области современного катализа приполучении возобновляемых источников энергии, а также требуют дальнейшее исследование. Полученные данные способствуют решению вопросов развития отечественного производства катализаторов.

Ключевые слова: перовскит, флюорит, композиты, биомасса, водород.

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