Research Article

Symbat Muratbekovna Naurzkulova, Marina Vasilievna Arapova, Arcady Vladimirovich Ishchenko, Tamara Andreevna Krieger, Andrei Aleksandrovich Saraev, Vasilii Vasilievich Kaichev, Vladimir Alekseevich Rogov, Aleksei Vyacheslavovich Krasnov, Bakytgul Kabykenovna Massalimova, Vladislav Aleksandrovich Sadykov*

Ni–Ru-containing mixed oxide-based composites as precursors for ethanol steam reforming catalysts: Effect of the synthesis methods on the structural and catalytic properties

<https://doi.org/10.1515/chem-2021-0062>

received December 8, 2020; accepted May 25, 2021

Abstract: Ethanol steam reforming catalyst's precursors, i.e., nanocomposites of complex oxides with the general formula $[\text{Pr}_{0.15}\text{Sm}_{0.15}\text{Ce}_{0.35}\text{Zr}_{0.35}\text{O}_2 + \text{LaMn}_{0.45}\text{Ni}_{0.45}\text{Ru}_{0.1}\text{O}_3]$ (1:1 by mass), were synthesized by three different methods. It was shown that two synthesis methods – ultrasonic dispersion and sequential polymeric method, lead to the formation of the nanocomposite perovskite–fluorite system with the specific surface area up to 50 m²/g. Reduction of samples at 400–500°C lead to the formation of Ni–Ru alloy nanoparticles strongly bound with the surface of oxide nanocomposite. Catalytic tests in ethanol steam reforming reaction at 500–600°C showed the highest specific activity

of the sample prepared by the sequential polymeric method due to the location of Ni- and Ru-containing perovskite mainly on the surface of the composite providing a high concentration of active metal centers. At higher temperatures for all samples, ethanol conversion approached 100% with hydrogen yield varying in the range of 65–75%. A study of spent catalysts confirmed the absence of carbon deposits after long-term catalytic tests at 650°C.

Keywords: perovskite, fluorite, ethanol, reforming, hydrogen

1 Introduction

To date, hydrogen is the most environmentally friendly fuel for various energy and heat generators (fuel cells, internal combustion engines and mobile power plants) [1]. In context of the green energy of the future, hydrogen is associated with a promising technology of electrochemical generators based on solid oxide fuel cells (SOFCs) with internal or external reformer of fuels, whose main qualities are environmental friendliness, mobility and high efficiency [2]. Moreover, due to fuel source flexibility, such devices can successfully provide reforming of various carbon-containing fuels, including bio-renewable ones [3]. Among others, a great attention is paid to the ethanol steam reforming process [4]. Since the catalyst for internal fuel reforming in SOFC is a multifunctional layer supported on the anode, it must satisfy many requirements: (1) activity in the reaction of steam reforming of oxygenates (breaking C–C and C–H bonds), (2) thermochemical stability (resistance to sintering and carbonization), (3) compatibility with anode layers (stability to delamination and cracking) and (4) mixed ionic-electron conductivity [5]. Today, it is known that some

* **Corresponding author: Vladislav Aleksandrovich Sadykov**, Department of Heterogeneous Catalysis, Federal Research Center, Boreskov Institute of Catalysis, Lavrentiev Ave. 5, Novosibirsk 630090, Russia; Department of Natural Sciences, Novosibirsk State University, Pirogova St. 2, Novosibirsk 630090, Russia, e-mail: sadykov@catalysis.ru, tel: +7-383-330-8763

Symbat Muratbekovna Naurzkulova, Bakytgul Kabykenovna

Massalimova: Department of Chemistry and Chemical Technology, M. Kh. Dulaty Taraz Regional University, Tole Bi Str., 60, 080000, Taraz, Kazakhstan

Marina Vasilievna Arapova, Aleksei Vyacheslavovich Krasnov:

Department of Heterogeneous Catalysis, Federal Research Center, Boreskov Institute of Catalysis, Lavrentiev Ave. 5, Novosibirsk 630090, Russia

Arcady Vladimirovich Ishchenko, Tamara Andreevna Krieger, Andrei Aleksandrovich Saraev, Vasilii Vasilievich Kaichev, Vladimir

Alekseevich Rogov: Catalyst Research Department, Federal Research Center, Boreskov Institute of Catalysis, Lavrentiev Ave. 5, Novosibirsk 630090, Russia

nanocomposite materials, including complex oxides of transition and rare-earth elements (RRE) with the structures of perovskite, fluorite, or spinel, have the aforementioned properties [4–7]. In the early works of our laboratory, perovskite–fluorite based nanocomposites with very promising characteristics in fuel reforming were developed [8–10]. In the present study, $\text{Pr}_{0.15}\text{Sm}_{0.15}\text{Ce}_{0.35}\text{Zr}_{0.35}\text{O}_2$ and $\text{LaMn}_{0.45}\text{Ni}_{0.45}\text{Ru}_{0.1}\text{O}_3$ were chosen as composite components. Incorporation of rare earth cations (La^{3+} , Sm^{3+} , Gd^{3+} and $\text{Pr}^{3+/4+}$) into ceria-zirconia solid solution stabilizes its structure and affects oxygen mobility/acid–base surface properties [26]. Ni-containing perovskite-type oxides are well-known catalyst's precursors for the hydrogen production reactions. A high activity of catalysts based on substituted perovskite precursors $\text{LaNi}_{1-x}(\text{M})_x\text{O}_3$ ($\text{M} = \text{Mn}$, Fe , Ru) in reforming reactions was shown in previous studies [11–15]. The methods of nanocomposite materials synthesis should provide a high chemical uniformity of obtained complex oxides along with their high dispersion. It can be coprecipitation, hydrothermal method, solvothermal method, sol–gel–citrate and ester polymer precursors (Pechini), microemulsions, microwave method, sonochemical method, solution combustion and spray pyrolysis reactions [16].

In this article, the results of optimization of the perovskite–fluorite nanocomposite synthesis by elucidating its effect on textural, structural, surface and catalytic properties of the obtained materials are presented. Nanocomposites were prepared by three methods — the sequential polymeric method, ultrasonic dispersion of the as-prepared complex oxides in isopropanol with addition of surfactant and the one-pot polymeric method. Features of interaction between components affecting their texture, structural features, surface properties and reactivity were elucidated by N_2 adsorption, XRD and HRTEM with EDX, XPS, CO chemisorptions and H_2 -TPR; catalytic properties were studied in ethanol steam reforming. The best catalytic activity along with the coking stability was demonstrated by nanocomposite prepared by the sequential polymeric method due to optimized interaction between components providing the highest concentration of surface metal centers strongly interacting with support and high reactivity of surface oxygen species.

2 Methods

2.1 Catalysts synthesis

$\text{Pr}_{0.15}\text{Sm}_{0.15}\text{Ce}_{0.35}\text{Zr}_{0.35}\text{O}_2$ (PSCZ) and $\text{LaMn}_{0.45}\text{Ni}_{0.45}\text{Ru}_{0.1}\text{O}_3$ (LMNR) were synthesized by the organic polymeric precursor method [15,16], which is the modified Pechini

method [17]. The synthesis was performed using crystalline hydrates of $\text{Pr}(\text{NO}_3)_3$ (Vecton), $\text{Sm}(\text{NO}_3)_3$ (Vecton), $\text{Ce}(\text{NO}_3)_3$ (Vecton), $\text{La}(\text{NO}_3)_3$ (Vecton), $\text{Mn}(\text{NO}_3)_2$ (NevaReactiv), $\text{Ni}(\text{NO}_3)_2$ (Vecton), ZrOCl_2 (Reakhim) and crystalline anhydrous RuOCl_3 (Reakhim). For organic polymer formation monohydrate of citric acid $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (Vecton), ethylene glycol $\text{C}_2\text{H}_6\text{O}_2$ (Reakhim) and ethylene diamine $\text{C}_2\text{H}_8\text{N}_2$ (Reakhim) were used. All reagents were of chemical pure grade. Before synthesis, the exact molar masses of crystalline hydrates were refined by thermal analysis to determine the actual water content. The reagents with molar ratios of $v_{(\text{citric acid})}:v_{(\text{ethylene glycol})}:v_{(\text{ethylene diamine})}:\Sigma v_{(\text{metals})} = 3.75:11.25:3.75:1$ were chosen. The total moles of metals were calculated according the formula $\Sigma v_{(\text{metals})} = \Sigma i \cdot v_{(\text{oxide})}$, where i and $v_{(\text{oxide})}$ are the cation's indices in the chemical formula and the number of moles of synthesized complex oxide.

All process was carried out under continuous stirring. Citric acid was dissolved in ethylene glycol under weak heating (60–80°C). The solution was cooled to a room temperature and supplemented with a necessary amount of crystalline metal salts: $\text{Pr}(\text{NO}_3)_3$, $\text{Sm}(\text{NO}_3)_3$, $\text{Ce}(\text{NO}_3)_3$ and ZrOCl_2 hydrates for $\text{Pr}_{0.15}\text{Sm}_{0.15}\text{Ce}_{0.35}\text{Zr}_{0.35}\text{O}_2$ and $\text{La}(\text{NO}_3)_3$, $\text{Mn}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$ and RuOCl_3 for $\text{LaMn}_{0.45}\text{Ni}_{0.45}\text{Ru}_{0.1}\text{O}_3$. After salts were completely dissolved, ethylene diamine was added dropwise to further polymerize the organic precursors. A complete homogenization took 2 h. The resulting mixture was evaporated to obtain a thick polymer, which was grinded in a mortar and calcined in air at 700°C for 4 h.

Composite samples [$\text{Pr}_{0.15}\text{Sm}_{0.15}\text{Ce}_{0.35}\text{Zr}_{0.35}\text{O}_2$]: [$\text{LaMn}_{0.45}\text{Ni}_{0.45}\text{Ru}_{0.1}\text{O}_3$] = 1:1 (by mass) were prepared by three methods and were labeled as Sim1, Sim2 and Sim3. Details of preparation methods are presented. Sim1: 2.5 g of crystalline oxide ($\text{Pr}_{0.15}\text{Sm}_{0.15}\text{Ce}_{0.35}\text{Zr}_{0.35}\text{O}_2$), prepared by the modified Pechini method, calcined under air at 700°C was added to the polymer (acetic acid + ethylene glycol) solution of $\text{La}(\text{NO}_3)_3$, $\text{Mn}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$ and RuOCl_3 during the modified Pechini synthesis of 2.5 g $\text{LaMn}_{0.45}\text{Ni}_{0.45}\text{Ru}_{0.1}\text{O}_3$. Resulting suspension of PSCZ oxide in a polymer matrix with La, Ni, Mn and Ru salts was stirred for 2 h, evaporated to obtain a thick polymer and grinded and calcined in air at 700°C for 4 h. Sim2: 2.5 g of $\text{Pr}_{0.15}\text{Sm}_{0.15}\text{Ce}_{0.35}\text{Zr}_{0.35}\text{O}_2$ and 2.5 g of $\text{LaMn}_{0.45}\text{Ni}_{0.45}\text{Ru}_{0.1}\text{O}_3$ (prepared by the modified Pechini method) were added into solution of 1.5 mL polyvinyl butyral (5%) and 70 mL isopropanol and stirred using ultrasonic dispersion for 40 min. The suspension obtained was dried to complete evaporation of the solvent and calcined at 700°C for 2 h. Sim3: This is the one-pot method where salts of La, Pr, Sm, Ce, La, Ni, Mn and Ru in quantities necessary to obtain [$\text{Pr}_{0.15}\text{Sm}_{0.15}\text{Ce}_{0.35}\text{Zr}_{0.35}\text{O}_2$]: [$\text{LaMn}_{0.45}\text{Ni}_{0.45}\text{Ru}_{0.1}\text{O}_3$] = 1:1 by mass composition were added

to the polymer gel of acetic acid + ethylene glycol, keeping the molar ratio $V_{(\text{citric acid})}:V_{(\text{ethylene glycol})}:V_{(\text{ethylene diamine})}:\Sigma V_{(\text{metals})} = 3.75:11.25:3.75:1$. After salts were completely dissolved, ethylene diamine was added dropwise to further polymerize the organic precursors, and solution was stirred for 2 h. The resulting mixture was evaporated to obtain a thick polymer, which was grinded in a mortar and calcined under air at 700°C for 4 h.

For catalytic studies, the resulting powders were pressed into pellets followed by crushing and sieving to the 0.25–0.5 mm grain size fraction.

2.2 Texture, structural and surface properties, reactivity and catalytic activity

The specific surface area of samples was evaluated by the Brunauer–Emmet–Teller (BET) method by recording nitrogen physical adsorption at the liquid nitrogen temperature using an ASAP-2400 (Micromeritics Instrument Corp., Norcross, GA, USA) automated volumetric adsorption unit. Before the analysis, samples were outgassed at 150°C for 4 h at a pressure of 1×10^{-3} Torr (~ 0.1 Pa). The obtained adsorption isotherms were used to calculate the specific surface area. The nature of crystallographic phases in oxides was characterized by X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HR TEM). Diffraction patterns were observed using a Bruker Advance D8 diffractometer with a $\text{CuK}\alpha$ source (2θ range 20–85°, step size 0.05 and accumulation time 3 s). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and high-resolution transmission electron microscopy (HRTEM) images of as-prepared samples were obtained with a JEM-2200FS transmission electron microscope (JEOL Ltd., Japan, acceleration voltage 200 kV, lattice resolution 1 Å) equipped with a Cs-corrector and an EDX spectrometer (JEOL Ltd., Japan). The minimum spot diameter for the step-by-step line or mapping elemental EDX analysis was ~ 1 nm with a step of about 1.5 nm. Identification of the obtained phases and quantitative calculations were done using the ICDD database.

The surface chemical composition of samples was studied by the X-ray photoelectron spectroscopy (XPS) on an electronic spectrometer SPECS Surface Nano Analysis GmbH (Germany). The spectrometer is equipped with a PHOIBOS-150-MCD-9 hemispherical analyzer, as well as an XR-50 X-ray source with a double Al/Mg anode. The samples were analyzed after reduction in 5 vol% H_2/N_2 at 650°C for 1 h. After reduction, samples were discharged

from the reactor and contacted with air being partially oxidized. Powders of samples were fixed at the holder with the help of the two-sided conducting scotch tape. The binding energy (E_B) scale was calibrated using the $\text{Ce3d}_{5/2}$ cerium line ($E_B = 916.7$ eV). Determination of the relative abundance of elements in the analysis zone was carried out from the integral intensities of XPS lines taking into account the photoionization cross sections of the corresponding terms [18]. For a detailed analysis of the spectra, the spectra were decomposed into individual components. After subtracting the background by the Shirley method, the experimental curve was expanded into a number of lines corresponding to the photoemission of electrons from atoms in different chemical environments. Data processing was carried out using the CasaXPS software package [19]. The peak shapes are approximated by a symmetric function obtained by multiplying the Gaussian and Lorentz functions.

To estimate the number of accessible surface metal sites, experiments with CO chemisorptions at decreased (-40°C) temperatures followed by its temperature-programmed desorption were carried out in a flow setup with a quartz tubular reactor (inner diameter 4 mm). Before chemisorption, samples were heated for 20 min from room temperature to 600°C in the stream of He (5 L/h) and then reduced by the mixture of 3% H_2 in He during 1 h. Then, samples were cooled to -40°C in the stream of He and kept at this temperature for 30 min in the stream of 5% CO in He. After switching to the stream of He, samples were heated at 50°C with the temperature ramp of $0.4^\circ/\text{s}$ and then at 400°C with the temperature ramp of $\sim 2^\circ/\text{s}$. The analysis of desorbed CO and CO_2 concentrations was carried out using a gas analyzer (Sibmicroreactor) with the thermal conductivity detector.

Material reactivity was characterized by temperature-programmed reduction by H_2 (TPR- H_2) (10% H_2 in Ar, the feed rate 2.5 L/h and the temperature ramp from 25 to 900°C at $10^\circ/\text{min}$) in a flow kinetic setup with a quartz U-shaped reactor equipped with a Tsvet-500 chromatograph and a thermal conductivity detector.

Ethanol steam reforming (ESR) was conducted in a continuous flow fixed-bed quartz reactor under atmospheric pressure in the temperature range of 500–800°C. A total of 30 mg of catalyst (0.25–0.5 mm fraction) was loaded and sandwiched between two quartz wool layers. Before the activity test, the catalyst was reduced with 5 vol% H_2/N_2 (100 mL/min) at 800°C for 1 h. EtOH and H_2O mixture ($\text{H}_2\text{O}/\text{EtOH}$ mole ratio of 4) supplied by a liquid pump was heated in the evaporator up to 120°C, and this vapor was mixed with N_2 stream from the mass-flow controller, yielding a gas composition

EtOH:H₂O = 1:4, C(EtOH) = 2%, C(H₂O) = 8 vol% at contact time 10 ms. The outlet products were analyzed by gas chromatography. Ethanol conversion $X_{C_2H_5OH}$, hydrogen yield Y_{H_2} and products selectivities S_i were calculated according to the formulas:

$$X_{C_2H_5OH}(\%) = \frac{C_{C_2H_5OH}^0 - C_{C_2H_5OH}}{C_{C_2H_5OH}^0} \cdot 100,$$

$$Y_{H_2}(\%) = \frac{C_{H_2}}{6 \cdot C_{C_2H_5OH}^0} \cdot 100,$$

$$S_i(\%) = \frac{v_i C_i}{2(C_{C_2H_5OH}^0 - C_{C_2H_5OH})} \cdot 100$$

where $C_{C_2H_5OH}^0$ is the initial ethanol concentration, v_i – number of carbon atoms in molecule and i = CO, CO₂, CH₄, C₂H₆, C₂H₄O, C₂H₄.

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

3 Results

3.1 Textural and structural features

Table 1 presents sample's designations, chemical composition, specific surface area (S_{BET}) and short description of the synthesis method. As presented in Table 1, fluorite sample possesses much higher specific surface area compared to that of perovskite due to a higher sinterability of the latter [15,20]. Nanocomposites are characterized by intermediate values of specific surface areas. The lowest area was demonstrated by Sim1 sample due to sintering of perovskite surface layers supported on PSCZ fluorite. A higher surface area somewhat exceeding the expected average value for the mechanical mixture of two phases

was found for nanocomposite prepared by ultrasonic dispersion.

The highest surface area was revealed for one-pot sample, which could be due to the absence of the perovskite phase in its composition (*vide infra*).

3.1.1 XRD

The XRD patterns of samples are shown in Figure 1a. The pattern of Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O₂ corresponds to a fluorite with the cubic structure. Peak broadening is a typical phenomenon for the doped Ln_{1-y}Zr_yO₂ (Ln = Ce, Pr, Sm), which indicates mixed oxide formation with defects induced by the lattice sites occupation by cations with different ionic radii [20]. Two small peaks indicate insignificant admixtures of zirconium oxides: peak at 30° corresponds to the tetragonal ZrO₂ phase, while peak at 32° corresponds to ZrO₂ with the monoclinic structure (Figure 1c). Results for LaMn_{0.45}Ni_{0.45}Ru_{0.1}O₃ match with the typical diffraction pattern of LaMnO_{3.11} rhombohedral perovskite phase (X-Ray diffraction database Powder Diffraction File PDF #50-0297). Low intensity peak at 28.1° indicates the presence of a minor amount of ruthenium oxide (Figure 1c).

The XRD data of composites indicate the formation of perovskite and fluorite phases in Sim1 and Sim2 samples (Figure 1a). Insignificant admixture of both tetragonal and monoclinic ZrO₂ for the Sim1 sample are determined by reflections at 30 and 31 degrees, respectively (Figure 1c). No diffraction peaks of ZrO₂ were detected for Sim2 sample. In addition, insignificant amounts of La₂NiMnO₆ impurities were found according to a small peak at 25.5° in all Sim1, Sim2 and Sim3 samples (Figure 1d). The presence or absence of the ruthenium oxide cannot be clarified because main peaks of this phase are superimposed on the peaks of fluorite at 28 and 35 degrees. Moreover, the perovskite peaks in Sim1 are shifted to larger angles

Table 1: Sample's composition, synthesis methods and specific surface area

Code	Composition	Synthesis method	S_{BET} (m ² /g)
Sim1	[Pr _{0.15} Sm _{0.15} Ce _{0.35} Zr _{0.35} O ₂]:[LaMn _{0.45} Ni _{0.45} Ru _{0.1} O ₃] 1:1 mass ratio	As-prepared PSCZ was introduced to a polymeric gel containing La, Mn, Ni and Ru salts	36
Sim2		As-prepared PSCZ and LMNR mixing in organic solvent by ultrasonic dispersion	49
Sim3		One pot	61
LMNR	LaMn _{0.45} Ni _{0.45} Ru _{0.1} O ₃	Modified Pechini	8
PSCZ	Pr _{0.15} Sm _{0.15} Ce _{0.35} Zr _{0.35} O ₂	Modified Pechini	75

Figure 1: XRD patterns of as-prepared samples. (a) Total patterns and (b–d) their enlarged fragments. P – perovskite phase, F – fluorite phase, R – Ruddlesden-Popper phase, M – monoclinic zirconia phase, T – tetragonal zirconia phase.

(indicates a decrease in the lattice parameter) and the perovskite peaks in Sim2 are shifted to the region of smaller angles due to the increase in the lattice parameter (Figure 1b). This implies redistribution of cations between perovskite and fluorite phases being specific for each preparation method. Also, perovskite peaks are more intense in Sim2 than in Sim1. This suggests a more disordered perovskite structure in Sim1 nanocomposite, which agrees with TPR- H_2 results (see Figure 5 below). This can be explained by a smaller sizes of perovskite particles in Sim1 nanocomposite whose sintering is hampered by the presence of highly dispersed fluorite particles (Table 1) in the mixture obtained after perovskite polymeric precursor decomposition as well as perovskite structure disordering at interfaces between perovskite–fluorite nanoparticles. This is apparently accompanied by redistribution of cations between phases, leading to shift of perovskite diffraction peaks as stated earlier.

The Sim3 sample exhibits broad peaks corresponding to the fluorite structure, while perovskite peaks are practically absent. The broad peak at 29° corresponding to the mixed fluorite phase shifts to smaller 2θ angles while peaks corresponding to tetragonal and monoclinic zirconia

phases appear (Figure 1c). This suggests that large La cations are incorporated into the fluorite phase increasing its lattice parameter, and hence, the perovskite structure forms only in a trace amount. A well-crystallized nickel oxide phase is present as well (Figure 1a). Since reflections corresponding to manganese oxides are not observed, Mn cations are apparently present as amorphous oxidic layers on the surface of fluorite phase although their inclusion into the bulk of fluorite particles is possible as well.

3.1.2 HR TEM

The HR TEM images (Figure 2) of Sim1 confirm the formation of well-crystallized perovskite and fluorite phases and show a developed interphase between them. For Sim2, the nanodomain structure of both fluorite and perovskite particles is observed. Due to a large size of perovskite particles and their rather weak interaction with smaller fluorite particles in the process of their ultrasound dispersed mixture drying and calcination at 700°C , perovskite and fluorite contacts are less frequent than in Sim1 sample. Sim3 morphology can be described as a

Figure 2: HR TEM images of as-prepared (a) Sim1, (b) Sim2 and (c) Sim3 (P – perovskite, F – fluorite) samples.

mixture of crystallized phases – fluorite phase nanoparticles, Zr oxides, layered particles with a structure close to the perovskite phase and as well as amorphous phases (Figure 2c). Crystallized NiO particles were not detected in Figure 2c; however, Figure 3b with the EDX analysis of another Sim3 sample area shows the uneven spatial distribution of nickel and a large particle of NiO. Results of EDX mapping for perovskite elements in nanocomposites are presented in Figure 3, and the analysis of the elemental composition in related areas is presented in Table 2. Based on these results, in micron-size areas, the highest concentration of elements corresponding to the perovskite phase is observed for Sim1 sample as expected. In small areas ~300 nm, nonuniformity of element distribution corresponding to both phases is observed for all samples. For Sim3 sample, tremendous nonuniformity of Ni distribution is revealed, indicating its segregation as rather big (up to micron size) NiO particles in some regions.

Thus, based on the XRD and TEM results of the nickel distribution uniformity and the extension of the perovskite–fluorite interface (which is known as fast oxygen

Table 2: Elemental composition of nanocomposite samples in regions a–d presented in Figure 3

Sample	Concentration, at%						
	La	Mn	Ni	Pr	Sm	Ce	Zr
Sim1_a	50.55	26.32	11.67	6.29	3.80	0.00	1.38
Sim1_b	38.04	22.85	32.16	4.30	2.41	0.00	0.23
Sim1_c	30.8	18.62	17.19	7.09	6.52	10.60	9.15
Sim1_d	45.02	16.07	13.80	7.34	5.79	6.57	5.41
Sim2_a	53.21	20.71	19.00	3.48	1.04	0.00	2.55
Sim2_b	17.32	11.87	6.29	8.47	10.49	23.65	21.91
Sim2_c	48.50	23.16	21.33	3.19	1.03	0.00	2.79
Sim2_d	32.93	16.4	13.40	6.52	6.23	12.15	12.36
Sim3_a	36.26	18.06	0.00	8.51	8.33	13.94	14.90
Sim3_b	14.36	7.67	59.75	3.65	3.00	5.35	6.21
Sim3_c	36.07	17.96	0.00	8.72	7.63	13.42	16.20
Sim3_d	37.33	16.08	0.00	9.01	7.24	14.52	15.81

transport pathway that helps to provide bifunctional mechanism of fuels reforming and minimize coke formation), it can be assumed that, from the point of view of

Figure 3: Elemental mapping superposition for Sim1, Sim2 and Sim3 samples. La – light blue, Mn – red and Ni – green. a,b,c,d-different regions of the same sample with their composition given in Table 2.

Table 3: Atomic ratios of elements in the near-surface layer

Sample	PrSmCeZr				LaMnNiRu	[La]/[Zr]	[Mn]/[Zr]
	[Pr]/[Sm]	[Ce]*	[Pr]*	[Sm]*	[Ru]**		
Sim1	2.29	1.86	1.14	0.50	0.10	11.72	1.83
Sim2	2.15	0.93	0.62	0.29	0.11	3.55	0.94
Sim3	2.17	1.26	0.68	0.31	0.06	3.92	0.73

*The ratios are normalized to [Zr].

**The ratios are normalized to [La].

catalytic activity, the method used for Sim1 nanocomposite preparation could be the most promising one.

3.2 Surface properties

XPS. Original XPS spectra with descriptions are given in Supplementary materials (Figures S1–S4). It should be noted that the La3d spectrum (La3d_{3/2} 850–860 eV) overlaps with the Ni2p_{3/2} spectrum (850–860 eV), which significantly complicates the identification of nickel [27,28]. For the catalysts under study, no photoelectronic peaks related to the Ni2p spectrum of nickel were found in the La3d spectrum even after reduction in hydrogen at 400°C. Treatment in hydrogen led to the removal of lanthanum carbonates, and the La3d spectra shifted noticeably, but no sharp peaks of metallic nickel were observed.

The relative concentrations (atomic ratios) of elements in the near-surface layer, determined on the basis of XPS data, are presented in Table 3. Based on Table 3, in the sequence of Sim1–Sim2–Sim3 samples relative concentration of Mn cations corresponding to domains of the perovskite phase decreases, which agrees with the EDX data. The binding energies are presented in Table 4. The

analysis of peaks shapes and positions given in Supplementary materials revealed that La, Sm and Mn cations are in 3+ state. For Zr cations, Zr3d_{5/2} peak is shifted to lower values (~181.5 eV) as compared with that in ZrO₂ (up to 183.2 eV) [29,30], which is explained by the effect of doping Pr and Sm cations. Pr cations are mainly (up to 85%) present in 4+ state, while three states of Ru are found: metallic (up to 50%) and two cationic states 4+ and 6+.

CO chemisorption. CO TPD spectra for Sim nanocomposites are shown in Figure 4. According to the results of FTIRS studies of CO adsorption on catalysts containing clusters of metals/alloys on complex oxides [21,22], bridging and terminal carbonyls bound with metal sites can be desorbed up to room temperature. Peaks at higher temperatures correspond to decomposition of formates, hydroxocarbonates or carbonates formed due to migration of carbonyl complexes from the metal sites to neighboring support sites [21,22,31]. Since these peaks are very weak for Sim1 sample with the surface mainly presented by perovskite layers, this implies association of formates/carbonates with Ce cations [31] present in higher amounts on the surface of Sim2 and Sim3 samples (Table 2). Carbonyls bound with coordinatively unsaturated cations of supports are removed by desorption even at 77 K [16,21,22], so their coverage was negligible at –40°C after purging by He,

Table 4: Binding energies (eV)

Sample	Zr3d _{5/2}	Ce3d _{3/2} -u'''	Pr3d _{5/2}	Sm3d _{5/2}	Ru3d _{5/2}	La3d _{5/2}	C1s
Sim1	181.5	916.7	933.6	1083.0	280.3 281.4 282.9	835.2	285.0
Sim2	181.5	916.7	933.3	1082.7	280.2 281.4 282.9	835.2	284.9
Sim3	181.5	916.7	933.6	1083.0	280.3 281.4 282.8	834.6	284.8

Figure 4: Temperature-programmed CO desorption from the surface of Sim1 (a), Sim2 (b) and Sim3 (c) nanocomposites. Red line – CO concentration (left axis), blue line – temperature (right axis).

which was checked in special experiments. Hence, peaks corresponding to CO desorption from metal surface sites in studied nanocomposites are situated in the temperature range from -20 to $+30^{\circ}\text{C}$ (Table 5), and the surface coverage by these sites does not exceed percent of monolayer. Although CO coverage by metal sites can be higher in the presence of CO in the gas phase [21,22], in our case, the most important is the relative concentration of these sites for studied nanocomposites.

Hence, the highest concentration of these sites for Sim1 agrees with EDX and XPS data on the highest content of surface cations corresponding to perovskite phase

containing Ni and Ru (*vide supra*) and is explained by specificity of this nanocomposite preparation.

The lowest T_{max} for Sim1 sample can be explained by domination of terminal carbonyls due to a small size of Ni–Ru clusters and their strong interaction with the reduced perovskite support [21,22]. The highest T_{max} for Sim3 sample can be explained by domination of bridging carbonyls due to the presence of large Ni particles generated by reduction of segregated NiO particles weakly interacting with the fluorite support (*vide supra*) [21,22].

3.3 Reducibility

Table 5: Estimation of the number of surface metal sites by amount of CO desorbed at low temperatures

Sample	T_{max} ($^{\circ}\text{C}$)	n_{CO} (10^{-6} mol/g _{cat})
Sim1	-20	3.4
Sim2	10	1.9
Sim3	30	0.55

TPR- H_2 patterns are shown in Figure 5. LMNR perovskite reduction curve has three main regions. At temperatures below 300°C , there are three overlapping peaks corresponding to the reduction of Ru^{3+} to Ru^0 , Ni^{3+} to Ni^{2+} and Mn^{4+} to Mn^{3+} . The broad peak with a maximum at 562°C corresponds to the reduction of Ni^{2+} to metallic nickel. The high-temperature peak of Mn^{2+} cation

Figure 5: The TPR- H_2 profiles of the LMNR and PSCZ, Sim1, Sim2 and Sim3 samples.

reduction into metallic manganese would not happen for manganese oxides below 900°C [23,24]. The PSCZ pattern shows the reduction profile typical for this type of oxide: there is a broad shoulder at 450° associated with the removal of surface forms of oxygen, and a broad peak at 580° followed by a plateau up to the highest temperatures, which indicates the reduction of bulk oxygen [20]. Sim1 and Sim2 samples have a similar behavior under reduction, Sim1 being more reactive in general. Ruthenium cations reduction begins at 202°C. This peak overlaps with peaks of Ni^{3+} to Ni^{2+} and Mn^{4+} to Mn^{3+} reduction with the maxima at 235°C for Sim1 and 262°C for Sim2, respectively [24,25]. The high-temperature peaks for Sim1 and Sim2 samples, as for LMNR, located at 775 and 795°C, respectively, correspond to the typical reduction of Mn^{3+} to Mn^{2+} in the perovskite structure [13,14]. The reduction of Ni^{2+} to metallic nickel occurs in the temperature range 400–500°C as evidenced by the wide peak in this area.

The TPR- H_2 profile for Sim3 looks typical for a mixture of Mn_xO_y and NiO oxides (all reduction peaks are below 500°C). There are two overlapped peaks with maxima at 237 and 296°C that can be attributed to the two-step reduction of MnO_2 : the first step corresponds to the reduction of MnO_2 to Mn_3O_4 and the second step indicates the further reduction of Mn_3O_4 to MnO . This result is in good agreement with the TPR- H_2 results of MnO_2 reported in the literature [23]. At temperature higher

than 400°C, the behavior is similar to PSCZ fluorite, where at these temperatures, the reduction plateau corresponds to the reduction of bulk oxygen of the oxide [10]. The absence of Mn_2O_3 peaks in the X-ray diffraction pattern and presence of classical for manganese oxide reduction peaks on the TPR- H_2 curves is explained by its amorphous state.

3.4 Catalytic properties in ethanol steam reforming

The hydrogen yield together with the selectivities for CO and CO_2 are shown in Figure 6. At temperatures above 600°C for Sim1 and Sim3 samples and above 650°C for Sim2 sample, the main reaction products are H_2 , CO and CO_2 , and the ethanol conversion remains stable at 100%.

For temperatures below 650°C, the kinetic parameters of the reaction were calculated. The effective reaction rate constant k_{eff} , $m^{-2} s^{-1}$, was calculated in the approximation that the reaction is of the first order in ethanol, taking into account the specific surface area of samples according to the formula [16]:

$$k_{eff} = - \frac{\ln(1 - X)}{\tau \times S_{BET} \times m_{cat}},$$

where X is ethanol conversion; τ is the contact time; s , S_{BET} and m_{cat} are specific surface area, $m^2 g^{-1}$, and weight, g, respectively, of samples used.

In accordance with the values obtained, the following regularities of catalytic activity were revealed. It was shown (Figure 7a) that the activation energy increases in a row $Sim1 < Sim2 < Sim3$ together with a corresponding decrease in the initial reaction rate, which indicates a decrease in the specific catalytic activity from Sim1 to Sim3 catalyst. The higher activity of Sim1 sample prepared by the sequential polymeric method is consistent with its structure. By using this synthesis method, the composite structure is formed in such a way that the perovskite phase with the active components (nickel and ruthenium) is finely dispersed and distributed mainly on the fluorite oxide surface, which helps to avoid the problem of blocking the active component in the bulk of the oxide. It results in a higher surface density of active metal sites as revealed by CO chemisorption. The specific catalytic activity of nanocomposites at 500°C (Figure 7a) apparently correlates with the number of surface sites estimated by CO chemisorptions (Table 5).

After temperature-programmed ethanol steam reforming experiments, the catalysts were oxidized to remove

Figure 6: Temperature dependence of ethanol conversion, hydrogen yield, CO and CO₂ selectivities for Sim1, Sim2 and Sim3 in ethanol steam reforming reaction.

Figure 7: (a) Linearized Arrhenius equation and activation energy E_a and (b) hydrogen yield at 650 °C in time-on-stream ethanol steam reforming tests.

residual carbon that can be possibly formed at low temperatures and reduced at 800 °C, and long-term tests were carried out at a constant temperature of 650 °C. It was shown (Figure 7b) that under these conditions, all catalysts do not lose their activity within 10 h, maintaining the

full conversion of ethanol and a constant level of hydrogen yield above 70%. Tests after the reaction did not reveal carbon deposits for all samples, which confirms a high oxidizing capacity of the support's oxides demonstrated by their TPR-H₂ patterns (Figure 5).

4 Conclusion

In this study, catalysts precursors based on perovskite–fluorite nanocomposites with the general formula $[\text{LaMn}_{1-x}\text{B}_x\text{O}_{3+\delta}/\text{Ln}_{1-y}\text{Zr}_y\text{O}_2]$ (1:1 by mass), B = Ni, Ru, Ln = Pr, Sm, Ce were synthesized by three different methods. Two synthesis methods — sequential polymeric method (formation of Ni- and Ru-containing perovskite from a polymer matrix in the presence of already formed fluorite oxide) and ultrasonic dispersion of as-prepared complex oxides in isopropanol with addition of surfactant — provide formation of nanocomposites with a developed interphase between phases. In the one-pot synthesis method from a polymer containing all cations, the perovskite phase is not formed due to La incorporation into the fluorite matrix, with inclusions of amorphous Mn oxides and NiO phase being present. As the result, the highest concentration of surface metal sites in reduced catalysts was revealed for nanocomposite prepared by the sequential polymeric method, while the lowest concentration was observed for samples prepared by the one-pot method. Catalytic activity of nanocomposites in ethanol steam reforming correlates with the surface density of metal sites. They are stable to coking and provide full conversion of ethanol and hydrogen yield above 70% at 650°C for 10 h.

Funding information: This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis project 0239-2021-0005 as well as by M. Kh. Dulaty Taraz Regional University, Taraz, Kazakhstan.

Author contribution: S. N.: investigation and writing; M. A.: investigation and writing; A. I.: investigation; T. K.: investigation; A. S.: investigation; V. K.: methodology; V. R.: investigation; A. K.: investigation, B. M.: supervision; V. S.: supervision and editing.

Conflict of interest: Vladislav Sadykov, who is the co-author of this article, is a current Editorial Board member of Open Chemistry. This fact did not affect the peer-review process. The authors declare no other conflict of interest.

Data availability statement: All data generated or analyzed during this study are included in this published article and its supplementary information files.

References

- [1] Wang M, Wang G, Sun Z, Zhang Y, Xu D. Review of renewable energy-based hydrogen production processes for sustainable energy innovation. *Glob Energy Interconnect*. 2019;2(5):436–43. doi: 10.1016/j.gloei.2019.11.019.
- [2] Edwards PP, Kuznetsov VL, David WIF, Brandon NP. Hydrogen and fuel cells: towards a sustainable energy future. *Energy Policy*. 2008;36:4356–62. doi: 10.1016/j.enpol.2008.09.036.
- [3] Bae J, Lee S, Kim S, Oh J, Choi S, Bae M, et al. Liquid fuel processing for hydrogen production: a review. *Int J Hydrog Energy*. 2016;41:19990–20022. doi: 10.1016/j.ijhydene.2016.08.135.
- [4] Laosiripojana N, Assabumrungrat S. Catalytic steam reforming of methane, methanol, and ethanol over Ni/YSZ: the possible use of these fuels in internal reforming SOFC. *J Power Sources*. 2007;163:943–51. doi: 10.1016/j.jpowsour.2006.10.006.
- [5] Xin X, Liu L, Liu Y, Zhu Q. Novel perovskite-spinel composite conductive ceramics for SOFC cathode contact layer. *Int J Hydrog Energy*. 2018;43:23036–40. doi: 10.1016/j.ijhydene.2018.10.159.
- [6] Duranti L, Sora IN, Zurlo F, Luisetto I, Licocchia S, Di Bartolomeo E. The role of manganese substitution on the redox behavior of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Mn}_{0.2}\text{O}_{3-\delta}$. *J Eur Ceram Soc*. 2020;40:4076–83. doi: 10.1016/j.jeurceramsoc.2020.04.017.
- [7] Liu Y, Jia L, Li J, Chi B, Pu J, Li J. High-performance Ni in-situ exsolved $\text{Ba}(\text{Ce}_{0.9}\text{Y}_{0.1})_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}/\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ composite anode for SOFC with long-term stability in methane fuel. *Compos B Eng*. 2020;193:108033. doi: 10.1016/j.compositesb.2020.108033.
- [8] Frolova-Borchert Y, Sadykov V, Alikina G, Lukashevich A, Moroz E, Kochubey D, et al. Nanocomposites comprised of doped cerium dioxide and lanthanum manganite for syngas production. *Solid State Ion*. 2006;177(26–32):2533–8. doi: 10.1016/j.ssi.2006.02.027.
- [9] Sadykov V, Mezentseva N, Alikina G, Bunina R, Rogov V, Krieger T, et al. Composite catalytic materials for steam reforming of methane and oxygenates: Combinatorial synthesis, characterization and performance. *Catal Today*. 2009;145:127–37. doi: 10.1016/j.cattod.2008.04.034.
- [10] Sadykov V, Mezentseva N, Alikina G, Bunina R, Pelipenko V, Lukashevich A, et al. Nanocomposite catalysts for internal steam reforming of methane and biofuels in solid oxide fuel cells: Design and performance. *Catal Today*. 2009;146:132–40. doi: 10.1016/j.cattod.2009.02.035.
- [11] Buciuman FC, Patcas F, Menezes JC, Barbier J, Hahn T, Lintz HG. Catalytic properties of $\text{La}_{0.8}\text{A}_{0.2}\text{MnO}_3$ (A = Sr, Ba, K, Cs) and $\text{LaMn}_{0.8}\text{B}_{0.2}\text{O}_3$ (B = Ni, Zn, Cu) perovskites 1. Oxidation of hydrogen and propene. *Appl Catal B*. 2002;35:175–83. doi: 10.1016/S0926-3373(01)00250-8.
- [12] Wei T, Jia L, Zheng H, Chi B, Pu J, Li J. LaMnO_3 -based perovskite with in-situ exsolved Ni nanoparticles: a highly active, performance stable and coking resistant catalyst for CO_2 dry reforming of CH_4 . *Appl Catal A*. 2018;564:199–207. doi: 10.1016/j.apcata.2018.07.031.
- [13] Pietri E, Barrios A, Goldwasser MR, Pérez-Zurita MJ, Cubeiro ML, Goldwasser J, et al. Optimization of Ni and Ru catalysts supported on LaMnO_3 for the carbon dioxide

- reforming of methane. *Stud Surf Sci Catal.* 2000;130:3657–62. doi: 10.1016/S0167-2991(00)80591-1.
- [14] Wang Y, Zheng Y, Wang Y, Wang H, Zhu X, Wei Y, et al. Evaluation of Fe substitution in perovskite LaMnO_3 for the production of high purity syngas and hydrogen. *J Power Sources.* 2020;449:227505. doi: 10.1016/j.jpowsour.2019.227505.
- [15] Pavlova S, Kapokova L, Bunina R, Alikina G, Sazonova N, Krieger T, et al. Syngas production by CO_2 reforming of methane using LnFeNi(Ru)O_3 perovskites as precursors of robust catalysts. *Catal Sci Technol.* 2012;2:2099–108. doi: 10.1039/C2CY20054F.
- [16] Sadykov VA, Arapova MV, Smal EA, Pavlova SN, Bobrova LN, Ereemeev NF, et al. Nanocomposite catalysts for transformation of biofuels into syngas and hydrogen: fundamentals of design and performance, application in structured reactors and catalytic membranes. *Catalysis.* 2019;31:216–41. doi: 10.1039/9781788016971-00216.
- [17] Pechini MP. Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor. Patent 3330697 U.S. 08.1963, patented 11.07.1967.
- [18] Scofield JH. Hartree-Slater subshell photoionization cross-sections at 1254 and 1487 eV. *J Electron Spectros Relat Phenom.* 1976;8:129–37. doi: 10.1016/0368-2048(76)80015-1.
- [19] Fairley N. Available from: www.casaxps.com
- [20] Sadykov V, Mezentsseva NV, Alikina GM, Lukashevich AI, Borchert YV, Kuznetsova TG, et al. Pt-supported nanocrystalline ceria-zirconia doped with La, Pr or Gd: factors controlling syngas generation in partial oxidation/autothermal reforming of methane or oxygenates. *Solid State Phenom.* 2007;128:239–48. doi: 10.4028/www.scientific.net/SSP.128.239.
- [21] Sadykov V, Pavlova S, Smal E, Arapova M, Simonov M, Mezentsseva N, et al. Structured catalysts for biofuels transformation into syngas with active components based on perovskite and spinel oxides supported on Mg-doped alumina. *Catal Today.* 2017;293–4:176–85. doi: 10.1016/j.cattod.2017.05.055.
- [22] Smal EA, Simonov MN, Mezentsseva NV, Krieger TA, Larina TV, Saraev AA, et al. Spinel-type $\text{Mn}_x\text{Cr}_{3-x}\text{O}_4$ -based catalysts for ethanol steam reforming. *Appl Catal B.* 2021;283:119656. doi: 10.1016/j.apcatb.2020.119656.
- [23] Ramesh K, Chen L, Chen F, Liu Y, Wang Z, Han YF. Re-investigating the CO oxidation mechanism over unsupported MnO , Mn_2O_3 and MnO_2 catalysts//. *Catal Today.* 2008;131:477–82. doi: 10.1016/j.cattod.2007.10.061.
- [24] Chen H, Li J, Cui W, Fei Z, Tian Q, Liu Q, et al. Precise fabrication of surface-reconstructed LaMnO_3 perovskite with enhanced catalytic performance in CH_4 oxidation. *Appl Surf Sci.* 2020;505:144112. doi: 10.1016/j.apsusc.2019.144112.
- [25] Zhang C, Zeng K, Wang C, Liu X, Wu G, Wang Z, et al. LaMnO_3 perovskites via a facile nickel substitution strategy for boosting propane combustion performance. *Ceram Int.* 2020;46:6652–62. doi: 10.1016/j.ceramint.2019.11.153.
- [26] Sadykov VA, Kuznetsova TG, Frolova-Borchert YV, Alikina GM, Lukashevich AI, Rogov VA, et al. Fuel-rich methane combustion: Role of the Pt dispersion and oxygen mobility in a fluorite-like complex oxide support. *Catal Today.* 2006;117:475–83. doi: <https://doi.org/10.1016/j.cattod.2006.06.017>.
- [27] Ramana CV, Vemuri RS, Kaichev VV, Kochubey VA, Saraev AA, Atuchin VV. X-ray photoelectron spectroscopy depth profiling of $\text{La}_2\text{O}_3/\text{Si}$ thin films deposited by reactive magnetron sputtering. *ACS Appl Mater Interfaces.* 2011;3:4370–3. doi: [org/10.1021/am201021m](https://doi.org/10.1021/am201021m).
- [28] Ledford JS, Houalla M, Proctor A, Gercules DM, Petrakis L. Influence of lanthanum on the surface structure and carbon monoxide hydrogenation activity of supported cobalt catalysts. *J Phys Chem.* 1989;93:6770–7. doi: 10.1021/j100355a039.
- [29] Bulavchenko OA, Vinokurov ZS, Afonassenko TN, Tsyrl'nikov PG, Tsybulya SV, Saraev AA, et al. Reduction of mixed Mn–Zr oxides: in situ XPS and XRD studies. *Dalton Trans.* 2015;44:15499–507. doi: 10.1039/C5DT01440A.
- [30] Tsunekawa S, Asami K, Ito S, Yashima M, Sugimoto T. XPS study of the phase transition in pure zirconium oxide nanocrystallites. *Appl Surf Sci.* 2005;252:1651–6. doi: 10.1016/j.apsusc.2005.03.183.
- [31] Jacobs G, Patterson PM, Graham UM, Sparks DE, Burtron H, Davis BH. Low temperature water-gas shift: kinetic isotope effect observed for decomposition of surface formates for Pt/ceria catalysts. *Appl Catal A Gen.* 2004;269:63–73.