Alumina and silica supported Ce–Fe–O systems obtained by the solution combustion

method and their performance in CO₂ hydrogenation to syngas

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ABSTRACT This study presents Ce–Fe–O systems supported on γ -Al₂O₃ or SiO₂ to enhance the reactivity of an oxygen-deficient CeFeO₃ perovskite phase, which are promising catalysts for the production of fuels and chemicals from CO₂ as feedstock. The synthesis was carried out by the glycine-nitrate solution combustion method at various fuel-to-oxidizer ratios, and with or without the addition of ammonium nitrate. The obtained composites were characterized by XRD, SEM, EDX, N₂-physisorption, H₂-TPR, and CO₂-TPD to study the relationship of physicochemical properties with catalytic CO₂ hydrogenation (rWGS) activity. γ -Al₂O₃ was found to be a more suitable support than SiO₂ due to its ability to form a higher content of the perovskite phase, significantly reduce the size of CeFeO₃ crystallites, and increase oxygen defectiveness and CO₂ adsorption capacity. Combustion in the presence of silica results in the binding of most of cerium into a silicate phase, which is inactive for rWGS.

Keywords perovskites, cerium orthoferrite, CeFeO₃, alumina, silica, solution combustion synthesis, glycine, carbon dioxide, CO_2 hydrogenation, rWGS

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1. Introduction

Reducing CO₂ concentrations in the atmosphere is a complex task which requires the search and development of optimal technologies for capturing and further converting CO₂ into useful chemicals for industrial processes or high value-added products [1]. In this regard, CO₂ hydrogenation is a suitable and actively studied method for recycling carbon dioxide, especially in a combination with hydrogen produced from renewable energy sources [2]. In particular, efficient conversion of CO₂ into synthesis gas (a mixture of CO and H₂) is possible at temperatures above 500 °C and atmospheric pressure through the reverse water gas shift (rWGS) reaction [3, 4]. In steam reforming of alcohols, the excess of which can become a serious problem for the biodiesel industry [5–7], rWGS can close the carbon cycle and reduce emissions of CO₂, which is a by-product [8].

This is hampered by the difficulties of finding and developing effective and low-cost catalytic materials with excellent thermal and long-term stability under redox conditions [9, 10]. Among various systems, perovskites, in particular ferrites, which have the above-mentioned advantages, can be promising materials for use in rWGS. This phenomenon is associated with enhanced self-diffusion of oxygen, the creation and regulation of oxygen defectiveness, the low energy barrier of the $Fe^{3+} \leftrightarrow Fe^{2+}$ transition under redox conditions, and the possibility of reuse of perovskites [11–14]. Partial reduction of ferrites, including under reaction conditions, allows one to *in situ* obtain highly dispersed metal nanoparticles from the perovskite phase [11, 12, 14].

Currently, ferrite-perovskite composite materials based on LaFeO₃ and its analogues doped at A and/or B sites are being widely studied for CO₂ hydrogenation [11–19]. A detailed study of such systems made it possible to establish that, firstly, increasing the number of oxygen vacancies contributes toward an increase of the CO₂ binding strength and the rate of CO₂ hydrogenation on the perovskite surface. Secondly, the partial substitution of A cations improves redox properties and the tendency to form oxygen vacancies. Thirdly, the presence of oxygen vacancies, FeO_x, and metal (Ni or Co) nanoparticles on the perovskite surface leads to a synergistic effect and a significant increase in rWGS activity of such systems.

However, simple ferrites with unsubstituted cations, especially cerium orthoferrite, have been studied much less as catalysts than substituted perovskites, despite the extensive literature on their preparation [20–26]. A feature of o-CeFeO₃

compared to other lanthanide ferrites is the possibility of a reversible $Ce^{3+} \leftrightarrow Ce^{4+}$ electronic transition, which can affect the redox properties of the perovskite and its defectiveness. Recently, a sample containing 94 wt% CeFeO₃, obtained by the solution combustion synthesis (SCS) method, was found to be highly active in rWGS [20]. Moreover, its activity is superior to LaFeO₃, previously studied in [18]. Compared to other methods to prepare cerium orthoferrite [27–32], the SCS method is much less labor-intensive and allows one to regulate the conditions for obtaining phase-pure and homogeneous powders. An important advantage of obtaining CeFeO₃ by this method is also the option of carrying out synthesis in a reducing atmosphere created by the gaseous products of a thermochemical reaction, which is important to prevent the oxidation of perovskite at T > 350 °C [20, 26].

The SCS synthesis approach has been already proven to be an effective tool for fine control of the microstructure and morphology of materials, which makes it possible to obtain foam-like [20, 26, 33, 34] or globular [33, 35] powders, including core-shell structure type [34, 36]. The main way of such control is to change the ratio of fuel and nitrates, the pH value and the final treatment temperature [37, 38]. For CeFeO₃ perovskite, the influence of the fuel-to-oxidizer ratio, the fuel type, as well as post-calcination temperature has been mainly studied [20, 39].

However, all these parameters did not change the extremely low specific surface area of perovskites. Therefore, another way to create porosity is the template-assisted SCS, where either a colloidal solution or powders (as external microstructure templates) with a developed pore system (Al_2O_3 , SiO_2 , etc.) are used [13, 37, 38]. The use of a colloid/template makes it possible to significantly moderate combustion by reducing the maximum temperature, and the reaction is localized in nanodomains between colloid/template particles [40]. This leads to a decrease in the crystallite size of the supported phase compared to its bulk form and homogeneously distributes the resulting target product throughout the volume of the support matrix [37, 40–44]. The obtained composite system can be additionally treated with alkali to remove the silicon- or aluminum-containing template [40–42, 45] or used in such form [43, 44, 46, 47], in which the template becomes a support for the second component, similar to traditional supported catalysts. For example, the use of a template leads to an increase in the photocatalytic activity of LaFeO₃ [46, 47].

It was previously found that even a mechanical mixture of 25 wt% $La_{0.75}Sr_{0.25}FeO_3$ perovskite with SiO₂ increases the CO yield compared to unsupported and CeO₂, ZrO₂, α -Al₂O₃, TiO₂ (rutile)-supported perovskites [48, 49]. This is explained by the formation of the smallest size of perovskite crystallites, which led to the highest content of oxygen defects and activity in rWGS compared to other supports. In the case of using Al₂O₃ and TiO₂, the observed decrease in activity of the composites is due to the encapsulation of perovskite nanoparticles, which prevents the adsorption of CO₂ and its participation in the catalytic cycle.

Thus, in this study, an oxide support (template) was used for the first time to obtain composites based on CeFeO₃ perovskite by the SCS method. The influence of the support type $(Al_2O_3 \text{ or } SiO_2)$ on the catalytic behavior of the Ce–Fe–O system in the rWGS process has been established. Additionally, the fuel-to-oxidizer ratio was varied by changing the amount of glycine or adding ammonium nitrate and compared with the bulk CeFeO₃ obtained previously in [20].

2. Experimental

2.1. Catalyst preparation

The CeFeO₃-containing system was prepared by solution combustion synthesis in the absence and the presence of a support, as well as ammonium nitrate (AN, 98.5 % (St.-Petersburg, Russia)). γ -Al₂O₃ was obtained by calcination of Pural SB Lot. N. 233144 (Sasol) pseudoboehmite at 700 °C for 2 h, silica gel of KSKG grade (Russia, the BET specific surface area of 190 m²/g and the total pore volume of 0.61 cm³/g [50]) was crushed to a fraction of 10 – 300 μ m.

In total, glycine ($C_2H_5NO_2$, 99.2 %, LenReactiv (St. Petersburg, Russia)) and the corresponding metal nitrates (MeN) $Ce(NO_3)_3 \cdot 6H_2O$ (99.8 %, Chemcraft (Kaliningrad, Russia); or 99.1 %, LenReactiv), $Fe(NO_3)_2 \cdot 9H_2O$ (98.3 %, LenReactiv; or 98.0 %, NevaReactiv (St.-Petersburg, Russia)), were dissolved in DI water in a wide 250 mL glass beaker to obtain one gram of cerium ferrite. For every gram of raw material there was 1 mL of water. In the solution, nitrates acted as oxidizing agents, and glycine as a fuel. Additionally, if necessary, γ -Al₂O₃ or SiO₂ (1 g per 1 g perovskite), and NH₄NO₃ were added. For 1 g of calculated perovskite, from 0.1 to 1 g of NH₄NO₃ was used. The bulk system is denoted as CeFe, and systems supported on Al₂O₃ and SiO₂ are denoted as CeFeAl and CeFeSi, respectively.

When the ratio between the reagents changes, the ratio of fuel-to-oxidizer (φ), calculated from the reducing and oxidizing valence states (RV and OV, respectively), also changes, as follows [38]:

$$\varphi = (-1) \frac{\Sigma(\text{coeff} \cdot \text{RV of fuel})}{\Sigma(\text{coeff} \cdot \text{OV of nitrate})}.$$
(1)

The methodology for calculating reducing and oxidizing valence states can be found in [51]. The resulting aqueous solution or suspension was heated on a 1 kW electric plate until boiling and subsequent combustion to form a solid powder. Previously, reproducibility was tested on two or three batches of samples [20, 33]. Reaction equations for each synthesis can be found in [20].

2.2. Characterization

XRD analysis was partially performed on a SmartLab 3 Diffractometer (Rigaku, Japan) equipped with 1D DteX250 detector and NiK_{β} filter at 30 mA, 40 kV, a 4 °/min scan speed, and a 0.01° step width. For other samples (CeFeAl (0.1 – 0.25 g AN) and CeFeSi) was used XRD-6100 diffractometer (Shimadzu, Japan) with CuK α radiation at 40 kV, 30 mA, scan speed of 1 °/min, step width of 0.02°, and *D*(divergence):*S*(scatter):*R*(receiving) = 1:1:0.3. The diffraction data were analyzed by the Rietveld method. The refinement procedure and software are similar to those given in [20].

SEM and energy-dispersive X-ray (EDX) spectroscopy were carried out on a VEGA 3 SBH microscope (TESCAN, Czech Republic) equipped with INCAx-act detector (Oxford instruments, UK).

 N_2 -physisorption data were obtained on Quantachrom's Autosorb-6iSA (USA) unit. The samples were preliminarily degassed at 250 °C under vacuum. The specific surface area and the total pore volume were determined using the BET equation, and the pore size distribution was determined by the NLDFT method.

H₂-TPR (temperature programmed reduction by H₂) and CO₂-TPD (temperature programmed desorption) were performed on a Chemosorb (SOLO, Russia) equipped with a TCD (thermal conductivity detector) and a MC7-200D quadrupole mass analyzer (Institute for Analytical Instrumentation of Russian Academy of Sciences). For H₂-TPR experiments, ca. 30 mg of a powder (calcined at 350 °C) was reduced from 100 to 800 °C at a 10 °/min rate under 20 mL/min of 10 vol% H₂/Ar (99.998 vol% purity). Propanol-2 cooled in the liquid N₂ was used as a water vapor trap.

Before CO₂-TPD, ca. 100 mg of a sample (calcined at 350 °C) was reduced *in situ* by a 50 vol% H₂/He flow (40 mL/min) at a ramp rate of 20 °/min to 510 °C and 10 °/min to 600 °C and held for 20 – 30 min. Then it was cooled to 350 °C in 50 % H₂/He (40 mL/min) and to 110 °C in He, after which it was saturated with CO₂ (CO₂/He flow, 10:90 vol%, 20 mL/min) for 20 min. After removing the physically adsorbed CO₂ by purging with He (20 mL/min), the sample was heated to 600 °C at a ramping rate of 10 °C/min.

2.3. Catalytic tests

The experiments were performed in a fixed-bed reactor at 1 atm and 600 °C. The reactor was a cylindrical quartz tube (37 cm in length, 15 mm in inner diameter), in which the sample was placed on a SiO₂ diffuser grid. The gases were fed into the reactor from top to bottom. A thermocouple pocket with a diameter of 5 mm was located in the center of the tube.

35 mg of the powder sample was initially heated in the air flow (50 mL/min) to 300 °C, then flushed with N₂ (99.999 vol. % purity, 40 mL/min) up to 400 °C. Thereafter, 50 vol% H₂ in N₂ was fed with a total flow of 80 mL/min for 0.5 h. After reduction, the sample was heated to 600 °C and exposed to the reactants (H₂:CO₂:N₂=1:1:1, 120 mL/min) at a weight hourly space velocity (WHSV) of 205.7 $\text{L}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ for 30 – 90 min. Nitrogen in the gas flow was used as the internal standard for gas chromatography, allowing establishing the mass balance. In order to prevent water from entering the GC, the outlet pipe passed through a cooling trap.

The outlet gases were analyzed on a GC-2010 Plus chromatograph (Shimadzu, Japan) with a TCD (capillary column RT-Msieve 5A (30 m, dinner = 0.53 mm) and capillary column Rt-Q-BOND (30 m, dinner = 0.53 mm); temperature program: $30 \degree C - 5 \min$; $30 - 60 \degree C$ with a heating rate $4 \degree/\min$; $60 - 100 \degree C$ with a heating rate $15 \degree/\min$; $100 - 150 \degree C$ with a heating rate $30 \degree/\min$; $150 \degree C - 3 \min$; $150 - 180 \degree C$ with a heating rate $5 \degree/\min$; $180 \degree C - 23.9 \min$).

Catalytic behavior was assessed by CO_2 conversion (X_{CO_2} , %):

$$X_{\rm CO_2} = \frac{\rm Molar flow C from CO}{\rm Molar flow C from CO_2 + CO} \cdot 100 \%,$$
(2)

where molar flow C from CO_2 or CO – molar flow of the compound multiplied by the number of carbon atoms in the compound, mol/h. Selectivity to CO in all test was 100 %.

3. Results and discussion

3.1. Phase composition and crystal structure

XRD patterns of various series of catalysts synthesized by the SCS method using glycine as a fuel are presented in Fig. 1. The first series (Fig. 1a) consists of the bulk Ce–Fe–O system (denoted CeFe) and several CeFe composites on alumina (CeFeAl) obtained at different fuel-to-oxidizer ratios (φ). A more detailed study of the bulk Ce–Fe–O system prepared with various fuels, additives, and φ was carried out in [20], therefore, it is presented here for comparison. The selected CeFe contains mainly orthorhombic CeFeO₃ perovskite (94 wt%) with a Pbnm space group (ICDD PDF-2 card No. 00-022-0166) and small amounts of iron and cerium oxides (Table 1). CeFeO₃ reflections observed for CeFeAl systems at 22.8°, 32.6 – 32.7°, 40.2 – 40.3°, 46.5 – 46.6°, and 58.1 – 58.2° 2 θ , corresponding to the planes (110), (112), (202), (004), and (024, 204), have more broadening and are shifted towards higher angles compared to bulk CeFe.

The second series (Fig. 1b) represents CeFeAl and CeFeSi systems synthesized with an additional oxidizing agent NH_4NO_3 in various quantities. Previous studies have shown [20] that the addition of ammonium nitrate (AN) to the reaction mixture promotes the formation of the target perovskite. Indeed, according to the data obtained by the Rietveld refinement method, samples obtained using AN have an increased content of CeFeO₃ (Table 1).

The crystallographic parameters of the synthesized systems based on CeFeO₃ are also presented in Table 1. The CeFeO₃ unit cell volume (239.93 \pm 0.01 Å³) in bulk CeFe was found to be in better agreement with the cell volume



FIG. 1. XRD patterns of bulk Ce–Fe–O (a) or supported CeFe on γ -Al₂O₃ and SiO₂ (a,b), synthesized by glycine–nitrate solution combustion using different ratios of fuel-to-oxidizer (φ) and the amounts of ammonium nitrate (AN). ICDD PDF-2 card No. for: orthorhombic(o)-CeFeO₃ – 00-022-0166; cubic(c)-CeO₂ – 01-075-8371; γ -Fe₂O₃ – 00-039-1346; γ -Al₂O₃ – 00-056-0457; hexagonal(h)-Ce_{4.67}Si₃O₁₃ – 00–043–441.

presented in [52] (238.9 Å³), than in [28] (241.3 Å³). The combustion of the glycine–nitrates mixture in the presence of Al₂O₃ leads to the formation of CeFeO₃ with an even smaller unit cell volume of 233.67 – 235.60 Å³ (Fig. 2a). Such a significant change in lattice parameters is confirmed by the shift of diffraction peaks towards larger angles compared to bulk CeFe. This can be the result of replacing Ce (site A) or Fe (site B) ions in the perovskite structure with aluminum having a smaller ionic radius ($_{VI}Al^{3+}$, 0.535 Å [53]) compared to $_{VIII}Ce^{3+}$ (1.143 Å) and $_{VI}Fe^{3+}$ (0.55 – 0.645 Å), which was previously shown in [54–56] for La_{1-x}Al_xFeO₃ and LaAl_yFe_{1-y}O₃. However, according to [55], Al³⁺ ions have a strong site preference for the B site.



FIG. 2. Dependence of the CeFeO₃ unit cell volume on the fuel-to-oxidizer ratio (φ) (a). Dependence of the CeFeO₃ crystallite size on φ (b) and CeFeO₃ content (c).

The unit cell parameter of the cubic phase of alumina also deviates upward from the reference value (Table 1), which indicates a distortion of the Al₂O₃ lattice. In this case, a shift in the peak position of the (440) plane towards lower angles 2θ is observed. The discrepancy between the ionic radii of rare earth elements and Al³⁺, leading to an extremely low equilibrium solubility limit of rare earth elements ~ 10^{-3} % [57], makes it possible to exclude the introduction of cerium ions into the Al₂O₃ matrix. Therefore, the most probable is the substitution of Al³⁺ by Fe³⁺ [58].

Interestingly, replacing the alumina support by silica gel under the same synthesis conditions negatively affects the content of the perovskite phase. Moreover, from previous studies of SiO₂-supported perovskite oxides, it is known that the interface region of the SiO₂-based composite is the most vulnerable to solid-phase reactions [41,49]. A more detailed examination of the range of $20 - 35 2\theta^{\circ}$ for CeFeSi (Fig. 1b) shows the formation of a secondary phase of cerium oxide silicate in a significant amount (17 wt% Ce_{4.67}Si₃O₁₃).

The size of crystallites in Ce–Fe–O based systems was also analyzed. With a decrease in the fraction of cerium ferrite, the mean size of perovskite crystallites also decreases by more than 2 times (Fig. 2b) depending on the synthesis

N	m(AN); n(AN)/ n(MeN)	φ	Phase composition according to the Rietveld method/corrected*, wt%					$D_1,$ nm:	D_2 , nm:	<i>D</i> ₃ , nm:	$D_4,$ nm:	$R_{wp}/$
1			o- CeFeO ₃	c- CeO ₂	γ - Fe ₂ O ₃	$\begin{array}{c} \gamma \text{-Al}_2\text{O}_3\\ (\text{SiO}_2^{**}) \end{array}$	CeSiO	$V_1, Å^3$	$a_2, Å$	$a_3, Å$	$a_4, Å$	R_e
Ref. v.			50 or 100			50 or 0		—; 241.31	—; 5.4126	—; 8.3342	—; 7.9142	
1	0	1	4/8	18/33	5/9	73/50	0	19.2; 234.83	8.7; 5.4088	10.4; 8.2901	5.3; 7.9153	2.7
2	0	1.25	29	16	5	50	0	30.2; 233.67	11.6; 5.4094	7.4; 8.3419	8.2; 7.9205	1.1
3	0	1.5	15/14	25/23	15/13	45/50	0	27.0; 234.80	12.5; 5.4100	8.9; 8.3216	9.1; 7.9106	1.0
4	1 g; 1.5	1.25	45/42	4/4	4/4	47/50	0	28.6; 235.60	17.8; 5.4050	5.8; 8.3192	5.1; 7.9229	1.0
5	0.5 g; 0.75	1.36	40/33	10/8	10/8	40/50	0	28.6; 233.73	14.9; 5.4095	6.8; 8.3469	8.7; 7.9461	1.1
6	0.25 g; 0.375	1.43	57/31	19/10	16/9	8/50	0	19.9; 234.11	8.5; 5.4062	4.9; 8.2790	20.1; 7.7264	1.3
7	0.1 g; 0.15	1.47	23	19	8	50	0	17.3; 234.73	6.9; 5.4049	6.6; 8.3049	3.0; 7.9320	1.1
8	0.5 g; 0.75	1.36	13/7	37/20	17/9	0/47**	32/17	13.7; 240.16	9.7; 5.4120	19.9; 8.3728		1.1
9	1 g; 1.5	1.25	96/94	4/4	0/2	0	0	69.1; 239.93	15.6; 5.3970			1.1

TABLE 1. Data on the phase composition, crystallite sizes, and lattice parameters of Ce–Fe–Al(Si) and Ce–Fe oxide systems obtained by the glycine–nitrate SCS method

Note: *correction of fitting inaccuracies based on the specified alumina content or including amorphous iron oxide according to the equation wt% (Fe₂O₃)= wt%(CeO₂)/2.156, where 2.156 is the CeO₂/Fe₂O₃ weight ratio obtained from CeFeO₃; **SiO₂ instead of Al₂O₃; ref.v. – a reference value (expected); m(AN) – the mass of NH₄NO₃; n(AN)/n(MeN) – the ratio of stoichiometric coefficients of ammonium nitrate and metal nitrates (Ce and Fe); φ – the fuel-to-oxidizer ratio; CeSiO – h-Ce_{4.67}Si₃O₁₃ (ICSD 9378); *D* – the mean crystallite size; 1 – o-CeFeO₃ (modified ICSD 93611); 2 – c-CeO₂ (ICSD 193169); 3 – γ -Fe₂O₃ (ICSD 247036); 4 – γ -Al₂O₃ (ICSD 66558); the ratio of the weighted (*R*_{wp}) and expected (*R*_e) R-factors characterizes goodness of fit, if the squared value is equal to one or constant the refinement procedure is complete.

conditions. In this case, a linear correlation is observed between the Ce ferrite content and the mean size of its crystallites (Fig. 2c).

3.2. Structural and textural properties

The results of N₂ physisorption measurements are presented in Fig. 3 and Table 2. Data corresponding to the alumina support are also included for comparison. All presented systems display a IV type isotherm (Fig. 3a), which is usually ascribed to mesoporous materials according to the IUPAC classification [59]. The bulk system based on CeFeO₃ per se is non-porous, and small volumes of mesopores are apparently formed due to secondary porosity, namely, aggregation of small crystalline particles [20]. Most pore sizes for Al₂O₃- and SiO₂-supported CeFe systems are less than 20 nm and are uniformly distributed (the average pore diameter (d_p) is 10 nm), while the pore size distribution for the perovskite-based system is relatively wide, with two maxima of ca. 15 and 40 nm (Fig. 3b). As expected, the total pore volume decreased after loading the support with the perovskite-containing system, which leads to a decrease in the peak height of the pore size distribution compared to pure alumina. In the presence of a high surface area support, the specific surface area (S_{BET}) and the total pore volume (ΣV_p) of the supported Ce–Fe–O systems are 92 – 123 m²/g and 0.32 – 0.34 cm³/g, respectively.

According to SEM, phases of cerium ferrite and secondary oxides formed during combustion, due to the large amount of released gaseous reaction products, are organized into a crystalline foam-like nanostructure (Fig. 4a), surrounding individual particles of the support (Fig. 4b,c). The surface atomic ratios of Ce:Fe:Al, given in Table 2, turned out to be higher than the corresponding theoretical values, which can be explained by the heterogeneity of phase distribution.



FIG. 3. N₂ physisorption isotherms and the pore size distribution for Al₂O₃, CeFe (1 g AN, $\varphi = 1.25$), CeFeAl (0.5 g AN, $\varphi = 1.36$), and CeFeSi (0.5 g AN, $\varphi = 1.36$). For CeFeAl, the desorption branch of the isotherm is not completely recorded.

TABLE 2. Elemental composition (in at%) according to the EDX analysis and textural characteristics for Al_2O_3 , Ce–Fe and Ce–Fe–Al(Si) oxide systems

Sample	Ce	Fe	Al	Ce:Fe:Al	S_{BET} , m ² /g	ΣV_p , cm ³ /g	d_p, nm
CeFe (1 g AN, $\varphi = 1.25$)	48.36	51.64	_	1:1.07	2.3	0.01	15
$\operatorname{CeFeAl}\left(\varphi=1\right)$	10.76	12.21	77.03	1:1.13:7.16			
CeFeAl ($\varphi = 1.25$)	10.59	11.88	77.53	1:1.12:7.32			
CeFeAl ($\varphi = 1.5$)	11.19	12.55	76.26	1:1.12:6.82			
CeFeAl (1 g AN, $\varphi = 1.25$)	13.02	14.36	72.62	1:1.10:5.58			
CeFeAl (0.5 g AN, $\varphi = 1.36$)	12.09	13.24	74.67	1:1.10:6.18	92	0.34	15
CeFeSi (0.5 g AN, $\varphi = 1.36$)					123	0.32	10
Al ₂ O ₃					200	0.50	10

EDX mapping of morphologically distinct areas showed that the CeFeAl sample consists of dark subangular particles (Fig. 5, area 1) and bright foam-like particles (Fig. 5, area 2). The dark particles were found to contain more aluminum than bright ones, which indicates the formation of different thicknesses of the Ce–Fe–O layer on the surface of alumina. Similar results were obtained for the silica-supported CeFe system.



FIG. 4. Microphotographs of as-prepared (a) CeFe (1 g AN, $\varphi = 1.25$), (b) CeFeAl ($\varphi = 1.5$), (c) CeFeSi (0.5 g AN, $\varphi = 1.36$)



FIG. 5. EDX spectroscopy elemental maps (Al, Ce, Fe, and O) for CeFeAl ($\varphi = 1.5$)

3.3. Reducibility

The presented systems contain elements that are prone to changes in the degree of oxidation under redox conditions. H_2 -TPR makes it possible to characterize the stability of catalysts, as well as to identify the features of reduction depending on the synthesis conditions, phase composition, etc. Fig. 6 presents hydrogen consumption curves for the samples listed in Table 1.



FIG. 6. H₂-TPR (left) and CO₂-TPD+MS (right) spectra for Ce–Fe and Ce–Fe–Al(Si) oxide systems (after preliminary calcination at 350 °C). In some cases, in H₂-TPR experiments, after 800 °C, the samples were cooled until the TCD signal reached the baseline. CO₂-TPD+MS was recorded at temperature from 110 °C to 600 °C.

It was previously shown that the cerium ferrite-rich sample (CeFe) is characterized by two-stage reduction at 200 – 415 °C and 415 – 600 °C [20]. This occurs due to the partial reduction of Fe³⁺ in Fe₂O₃ nanoparticles and on the CeFeO₃ surface to Fe²⁺ (Fe₃O₄) with its subsequent reduction to FeO and Fe⁰ at 415 – 600 °C, as well as surface Ce⁴⁺ to Ce³⁺ with additional formation of oxygen vacancies [20, 26]. The reduction profile of CeFe supported on SiO₂ is close to the reduction profile obtained for bulk CeFe. However, a more complex phase composition, low perovskite content and the presence of cerium silicate suggest that the main contribution to hydrogen consumption comes from unbound Fe₂O₃.

CeFeAl samples of both series (obtained with or without ammonium nitrate) are characterized by complex reduction profiles, namely, at temperatures above 600 °C the third reduction region appears. XRD data of CeFeAl (sample No. 5 in Table 1) after reduction at 800 °C showed that destruction of o-CeFeO₃ does not occur under these conditions and metallic

iron is present, which is absent after reduction at 600 °C. At the same time, metallic Fe was discovered for CeFeSi after reduction at 600 °C. This allows one to partially associate the observed peaks with reduction of bulk γ -Fe₂O₃ and/or a solid solution Al₂O₃(Fe³⁺) to Fe₃O₄, further reduction of which to FeO continues at temperatures up to 600 °C [20, 26].

A quantitative comparison of H₂-TPR results (Table 3) shows that increasing φ for CeFeAl systems, obtained with or without AN, increases the fraction of easily reducible components, as well as the overall reducibility of these systems due to an increase in dispersion of Fe₂O₃ and CeO₂ and the fraction of bound iron and cerium in the perovskite (Table 1). CeFeAl samples synthesized with AN at $\varphi = 1.36$ and $\varphi = 1.43$ can be considered optimal in terms of CeFeO₃ content and reducibility. The use of γ -Al₂O₃ compared to SiO₂ makes it possible to obtain a larger amount of CeFeO₃, as well as more highly dispersed and easily reduced phases.

Region	CeFe	$\begin{array}{l} \text{CeFeAl} \\ (\varphi = 1) \end{array}$	$\begin{array}{c} \text{CeFeAl} \\ (\varphi = 1.25) \end{array}$	$\begin{array}{c} \text{CeFeAl} \\ (\varphi = 1.5) \end{array}$	$\begin{array}{c} \text{CeFeAl} \\ (1 \text{ g AN}, \\ \varphi = 1.25) \end{array}$	CeFeAl (0.5 g AN, $\varphi = 1.36$)	$\begin{array}{c} \text{CeFeAl} \\ (0.25 \text{ g AN}, \\ \varphi = 1.43) \end{array}$	CeFeSi
I (200 – 475 °C)	34	39	40	28	35	40	39	31
II (475 – 600 °C)	66	18	19	38	15	14	19	69
III (600 – 825 °C)	_	43	41	34	51	46	42	0
Total amount H ₂ , mmol/g*	1.8	4.6	4.2	4.6	3.1	3.7	3.8	4.5

TABLE 3. Hydrogen consumption (% of peak area) in different temperature regions

Note. *For all samples (except of CeFe), the amount of consumed H₂ is calculated on 50 wt% Ce-Fe-O.

3.4. CO₂-TPD with mass-spectrometry

According to previous studies (see Introduction section), CO₂ adsorption is a critical step in the rWGS reaction, because it occurs at surface oxygen defects. Therefore, the CO₂-TPD method was used for studying the features of CO₂ desorption and characterizing the surface defects in the bulk and alumina- and silica-supported Ce–Fe–O systems, similar to other perovskite-based systems [15, 16, 18, 19, 48, 49]. Fig. 6 (right) shows the curves of changes in mass number signals over time (temperature from 100 to 600 °C) during TPD experiments for three different systems. Based on the known mass spectra of CO₂, CO, and H₂, the following correspondence can be established between m/z and the detected ions: m/z = 16 - 0· or O₂·· (separately or as part of CO₂ and/or CO spectrum), m/z = 28 - CO· (separately or as part of the CO₂ spectrum), $m/z = 44 - CO_2$ ·, $m/z = 2 - H_2$ ·. Thus, the amount of desorbed CO₂ (m/z = 44) increases in the following order: CeFeSi < CeFeAI.

The discrepancy between the profiles of m/z = 44 and m/z = 28 evidences the presence in the m/z = 28 signal of a contribution from CO desorption, caused by the reaction between adsorbed CO₂ and oxygen vacancies. The amount of desorbed CO (m/z = 28) and O/O₂ (m/z = 16) increases in the order CeFeSi < CeFe < CeFeAl, suggesting a higher number of oxygen vacancies in CeFe supported on γ -Al₂O₃. In [49], the opposite result was obtained for LaFeO₃, which, as the authors explained, takes place due to the higher energy of vacancy formation in the presence of Al₂O₃ compared to SiO₂. The difference in the results with the data obtained in this study is apparently due to using a different synthesis method. This led to different regularities of interaction between the system components, which, in turn, affected the amount of formed CeFeO₃.

Calculation of the amount of desorbed CO₂, CO, and O/O₂ per S_{BET} shows that the surface density of oxygen vacancies increases in the order: CeFeSi < CeFeAl < CeFe, which corresponds to the CeFeO₃ content. At the same time, the amount of desorbed hydrogen remaining on the surface after the preliminary reduction stage increases in the order from CeFe to CeFeAl, which coincides with the amount of consumed hydrogen according to H₂-TPR data (Table 3). Apparently, this is associated with the formed solid solution of Fe³⁺ in γ -Al₂O₃, reduction of which leads to the formation of small metallic Fe nanoparticles that interact with neighboring phases and are capable of adsorbing hydrogen [60, 61]. Consequently, the low dispersion of the obtained Fe nanoparticles during the reduction of CeFeSi leads to a smaller amount of desorbed H₂.

3.5. Catalytic performance in CO₂ hydrogenation

The catalytic activity in terms of conversion of CO_2 to CO via the reverse water gas shift (rWGS) reaction for the bulk and supported Ce–Fe–O systems is presented in Fig. 7. It can be seen that perovskite-containing systems on alumina provide higher CO_2 conversion compared to the bulk CeFe system (Fig. 7a). In this case, there is no correlation with the content of the perovskite phase, because the bulk CeFe system contains 94 wt% CeFeO₃, while the alumina-supported



FIG. 7. Dependence of CO₂ conversion on time-on-stream (TOS) for the bulk Ce–Fe–O system and Al₂O₃- and SiO₂-supported CeFe obtained in the presence and the absence of NH₄NO₃ by the SCS method using glycine as a fuel (a,b). Conditions: 600 °C, H₂:CO₂:N₂ = 1:1:1, WHSV = 205.7 L·g⁻¹·h⁻¹. Influence of the total amount of desorbed CO₂ and the CeFeO₃ content in the Ce– Fe–O system on CO₂ conversion after 1 h of TOS (c).

systems – from 8 to 29 wt%. A slight increase in conversion for CeFeAl catalysts is observed with increasing the fuel-to-oxidizer ratio.

Combustion in the presence of ammonium nitrate (AN) also has a generally positive effect on the catalytic performance of alumina-supported CeFe systems (Fig. 7b). Maintaining the fuel-to-oxidizer ratio, the use of AN has a clear advantage in achieving higher CO₂ conversion on CeFeAl. However, adding 0.25 - 0.5 g of ammonium nitrate was found to be the most effective compared to smaller and larger amounts (0.1 g and 1 g, respectively). Interestingly, the silica supported CeFe system, also obtained with NH₄NO₃, has the lowest activity among the all presented catalysts.

The presented discussions correlate with the obtained CO_2 -TPD results, where combustion in the presence of SiO_2 reduces the number of oxygen vacancies in the system compared to CeFeAl (Fig. 7c). At the same time, having recalculated the fraction of perovskite in the Ce–Fe–O system, the following dependence with a maximum was obtained, as shown in Fig. 7c.

4. Conclusions

Currently, rare earth ferrites are increasingly finding their use in thermocatalytic redox processes, in particular in CO_2 hydrogenation to CO (the rWGS reaction) as a potential way to utilize carbon dioxide. This study demonstrates improved rWGS activity by using perovskite-based composites. The Ce–Fe–O (CeFe) systems supported on γ -Al₂O₃ (CeFeAl) or SiO₂ (CeFeSi) were prepared via the glycine-nitrate solution combustion synthesis (SCS), a simple, energy-and time-effective method for the production of nanomaterials.

 γ -Al₂O₃ has proven to be a suitable support for application in the SCS technology due to its ability to form a higher content of the CeFeO₃ perovskite phase compared to SiO₂. On silica, in turn, during combustion, most of cerium is bound into a low-active silicate phase, thereby limiting the formation of perovskite. On the contrary, reduction of a solid solution of Fe³⁺ in Al₂O₃, formed in small quantities, leads to the formation of small Fe nanoparticles capable of adsorbing hydrogen.

The use of alumina as a support significantly reduces the size of CeFeO₃ crystallites, but increases oxygen defectiveness and ability to CO₂ adsorption, which was determined by CO₂-TPD with mass spectrometry. CeFeAl has the highest amount of desorbed CO₂ (m/z = 44) and CO (m/z = 28) compared to bulk and SiO₂-supported CeFe. According H₂-TPR, in the presence of γ -Al₂O₃ makes it possible to obtain more highly dispersed and easily reduced phases compared to SiO₂. The obtained regularities serve as a prediction of the catalytic activity of these systems. The most active Ce–Fe–Al oxide system is obtained by using an additional oxidizer NH₄NO₃, the amount of which also affects φ and, consequently, CO₂ conversion.

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