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Control of Ni/$Ce_{1-x}M_xO_y$ Catalyst Properties Via the Selection of Dopant M = Gd, La, Mg. Part 2. Catalytic Activity

M.A. Kerzhentsev[1], E.V. Matus[1,2]*, I.Z. Ismagilov[1], O.B. Sukhova[1], P. Bharali[3], Z.R. Ismagilov[1,4]

[1]Boreskov Institute of Catalysis SB RAS, pr. Ak. Lavrentieva 5, 630090 Novosibirsk, Russia
[2]Novosibirsk State Technical University, pr. K. Marksa 20, 630073 Novosibirsk, Russia
[3]Tezpur University, Napaam, Tezpur - 784 028 Assam, India
[4]Institute of Coal Chemistry and Material Science FRC CCC SB RAS, pr. Sovetskiy 18, 650000 Kemerovo, Russia

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Abstract

To elucidate the role of support composition in autothermal reforming of ethanol (ATR of C_2H_5OH), a series of Ni catalysts (Ni content 2–15 wt.%) supported on different ceria-based oxides ($Ce_{1-x}Gd_xO_y$, $Ce_{1-x}La_xO_y$ and $Ce_{1-x}Mg_xO_y$; x = 0.1–0.9) were prepared. The synthetized materials were tested in ATR of ethanol at 200–700 °C. It was established that supports themselves show catalytic activity in ATR of C_2H_5OH and provide 10–15% yield of H_2 at 700 °C. Upon the increase of Ni content from 2 to 15 wt.% the temperature of 100% ethanol conversion decreases from 700 to 300 °C, hydrogen yield increases from 25 to 60%, the inhibition of C_2-C_3 by-products formation, as well as the promotion of decomposition of acetaldehyde occur. The enhancement of catalyst performance in ATR of C_2H_5OH has been observed in the next series of supports: $Ce_{1-x}Mg_xO_y < Ce_{1-x}Gd_xO_y < Ce_{1-x}La_xO_y$ and with a decrease of x to an optimal value that correlates with the improvement of Ni active component reducibility. At 600 °C on 10Ni/$Ce_{0.8}La_{0.2}O_{1.9}$ catalyst the H_2 yield of 50% was achieved at C_2H_5OH conversion of 100%. Stable and high performance of developed catalysts in ATR of C_2H_5OH indicates the promise of their use in the production of hydrogen.

1. Introduction

At present, the global energy consumption is increasing [1, 2] while the conventional hydrocarbon resources are depleting [3, 4]. Sustainable development of society implies a decrease in dependence on fossil fuels [5, 6]. Ethanol is one of the most significant chemicals in large quantity derived from biomass [7, 8]. The use of this renewable feedstock for producing hydrogen provides a green way of production of clean fuel of future [9, 10].

Autothermal reforming (ATR) of ethanol, combining the endothermic steam reforming (SR) reaction and the exothermic partial oxidation, is the most promising method of producing hydrogen, thanks to a favorable energy balance and a low rate of formation of carbon deposits on the catalyst [11–13]. According to the proposed reaction scheme for ethanol reforming [12, 13], the main reaction steps include ethanol dehydrogenation to acetaldehyde, its decomposition to methane and carbon monoxide, methane steam reforming and water gas shift reaction. However many side reactions might also occur, thus resulting in coke formation and less hydrogen yield. Possible side reactions involve ethanol dehydration to ethylene; its polymerization to coke; acetone formation via acetaldehyde condensation followed by decarboxylation; methane cracking and Boudouard reaction [12, 13]. So the task of the catalyst for ATR of ethanol is to maximize the yield of hydrogen and reduce the contribution of side reactions. The general requirements for catalysts include the following points [14–16]: catalyst should break C-C bond rather than promote the C-O bond activation; reform methane to generate hydrogen; activate water and oxygen to produce highly mobile oxygen species and to inhibit coke formation.

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*Corresponding author. E-mail: matus@catalysis.ru

Both transition metals (Ni, Co, Cu) and noble metals (Rh, Pt, Pd, Ir, Ag) have been applied as the active component for ethanol reforming while different oxides (Al_2O_3, CeO_2, La_2O_3, MgO, ZnO) are used as supports [17–21]. The nature of the metal and the support greatly affect the final product distribution [22]. According to the study of M/Al_2O_3 catalysts in oxidative steam reforming of ethanol [20], Ru-, Rh- and Ir-containing samples efficiently rupture the C-C bond of ethanol, resulting in the best hydrogen yield, while in the case of Co, Ni, Pd and Pt metals the dehydration of ethanol preferentially occurs with higher selectivity of ethylene formation. Often bimetallic catalysts have advantages over monometallic ones. It was demonstrated [23] that co-presence of Ni and Co in the catalyst composition favors the high hydrogen yield due to the enhanced reducibility of the bimetallic sample. The interaction of Rh and Pt in the bimetallic RhPt sample improved catalyst activity and stability against coking during ATR of C_2H_5OH [19]. It was shown that the quantity of carbon deposits formed in ATR reaction decreases in the following row of active metals: Ni >> Pt > Rh ~ RhPt [19]. However, the high price of noble based catalysts restricts their wide use.

It was shown that modification of supports is an effective way to control the catalyst performance in reforming of fuels [24–30]. This study is devoted to the elucidation of the role of support composition in autothermal reforming of ethanol over Ni/$Ce_{1-x}Gd_xO_y$, Ni/$Ce_{1-x}La_xO_y$ and Ni/$Ce_{1-x}Mg_xO_y$ catalysts. The regulation of support characteristics and, consequently, the catalyst properties is carried out through doping of ceria by Gd^{3+}, La^{3+}, Mg^{2+} cations of different molar portion (x is equal to 0, 0.1, 0.2, 0.5, 0.8, 0.9 and 1.0). To establish the structure-property-performance relationships, the results of catalyst tests in ATR of C_2H_5OH were correlated with physicochemical properties of catalysts.

2. Experimental

2.1. Catalyst preparation

The Ni/$Ce_{1-x}Gd_xO_y$, Ni/$Ce_{1-x}La_xO_y$ and Ni/$Ce_{1-x}Mg_xO_y$ catalysts (Ni content – 2–15 wt.%) were prepared by incipient wetness impregnation of appropriate supports (x is equal to 0, 0.1, 0.2, 0.5, 0.8, 0.9 and 1.0) with aqueous solutions of nickel nitrate. After impregnation, the samples were dried at 90 °C and calcined in air for 4 h at 500 °C. The number before nickel in the catalyst name corresponds to the Ni content (wt.%). The physicochemical properties of $Ce_{1-x}M_xO_y$ supports and Ni/$Ce_{1-x}M_xO_y$ catalysts were given and discussed in Part I of this article.

2.2. Catalytic activity measurements

ATR of C_2H_5OH was measured in a flow setup with a quartz reactor (14 mm i.d.) at atmospheric pressure, temperature 200–700 °C, a flow rate of 230 mL/min and the molar ratio between reagents $C_2H_5OH : H_2O : O_2 : He = 1 : 3 : 0.5 : 1$ according to the method described in [25].

3. Results and discussions

3.1. Catalytic activity of $Ce_{1-x}M_xO_y$ supports in ATR of C_2H_5OH reaction

The effect of chemical composition of prepared materials on their catalytic performance in ATR of C_2H_5OH is shown in Fig. 1–7 and Tables 1–3. Regardless of support composition over studied supports the ethanol conversion (X_{C2H5OH}) and hydrogen yield (Y_{H2}) rise with a growth of the temperature of process (Fig. 1).

The CeO_2 oxide and $Ce_{1-x}M_xO_y$ mixed oxides (x = 0.1–0.9) are characterized by higher ethanol conversion in the low-temperature region in comparison to X_{C2H5OH} over Gd_2O_3, La_2O_3 and MgO samples. However over all $Ce_{1-x}M_xO_y$ supports (x = 0–1) complete conversion of C_2H_5OH could be only obtained at 700 °C. Supports themselves provide 10–15% yield of H_2 at the reaction temperature of 600 °C and their performance has trend to improve in the following sequence: MgO < Gd_2O_3 ~ La_2O_3 < $Ce_{1-x}M_xO_y$ < CeO_2.

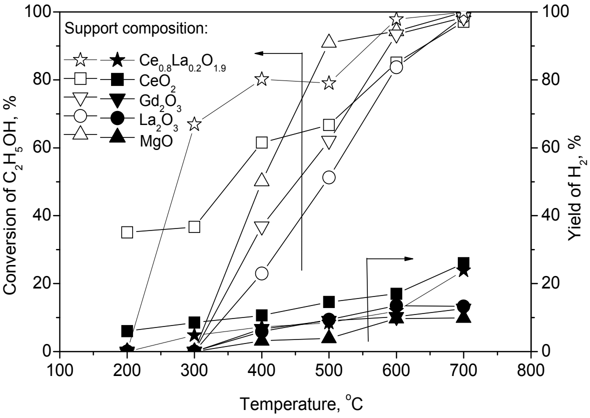

Fig. 1. Conversion of C_2H_5OH (open symbols) and yield of H_2 (bold symbols) in ATR of C_2H_5OH vs. reaction temperature over supports of different chemical composition.

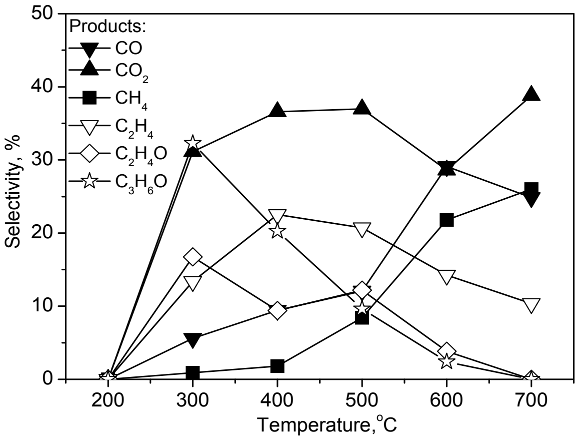

Fig. 2. Selectivity for C-products obtained in the ATR of C_2H_5OH over $Ce_{0.8}La_{0.2}O_{1.9}$ support.

Irrespectively of support composition, in addition to hydrogen, the formation of a wide range of carbon-containing products (C-products) was observed: acetaldehyde, acetone, ethylene, methane and carbon oxides. As a typical example, Fig. 2 shows the selectivity of C-products formation in the ATR of C_2H_5OH over $Ce_{0.8}La_{0.2}O_{1.9}$ support.

As a rule, with an increase of the reaction temperature the selectivity of C_2H_4O and C_3H_6O formation decreases, selectivity to CO and CH_4 increases, while those of the rest C-product have volcano-type dependence (Fig. 2). The C-product distribution is controlled by support composition (Table 1). In particular, at 600 °C Gd_2O_3 and La_2O_3 are noted for high selectivity of C_2H_4 and C_3H_6O formation, respectively, while at 400 °C MgO is highly selective to C_2H_4O which is subsequently decomposed to CO and CH_4. Among studied samples, the lowest selectivity of ethylene formation is observed over MgO which correlates with its basic properties. According to [13], in this case, the rate of C_2H_5OH dehydrogenation to acetaldehyde is faster than C_2H_5OH dehydration to ethylene. The C-product distribution over $Ce_{1-x}M_xO_y$ samples lies close to those on CeO_2 at a low molar fraction of the dopant (Table 1). Comparatively large selectivity of C_2-C_3 product formation and relatively low selectivity of CH_4 formation (Fig. 2, Table 1) indicate that supports have a weak capability of breaking the C-C bond in ethanol [31].

3.2. Catalytic activity of Ni/$Ce_{1-x}M_xO_y$ catalysts in ATR of C_2H_5OH reaction

The introduction of Ni in $Ce_{1-x}M_xO_y$ support changes the material performance in ATR of C_2H_5OH. As follows from Fig. 3a, at low Ni content the composition of products and its temperature dependence are still similar to those in the presence of support. Upon the increase of Ni content from 2 to 15 wt.% the inhibition of formation of ethylene and acetone occurs, as well as the promotion of decomposition of acetaldehyde (Fig. 3b, Fig. 4a). So at high Ni content (10–15 wt.%), irrespectively of the composition of $Ce_{1-x}M_xO_y$ support (x = 0.1–0.9), at 600 °C the amount of these compounds is below detected limits and C-products consist of CH_4 and carbon oxides only (Fig. 3b, Table 2).

Table 1

Performance of $Ce_{1-x}M_xO_y$ supports (x = 0, 0.2, 1) in ATR of C_2H_5OH

Sample	T, °C	X_{C2H5OH}, %	Y_{H2}, %	Selectivity, %					
				CO	CO_2	CH_4	C_2H_4	C_2H_4O	C_3H_6O
CeO_2	400	62	11	13	41	7	10	18	11
	600	85	17	27	32	14	10	16	1
Gd_2O_3	400	37	7	8	31	3	16	18	24
	600	93	10	28	21	14	26	4	7
La_2O_3	400	23	6	6	42	3	10	20	19
	600	84	14	20	29	18	13	6	14
MgO	400	50	3	7	42	2	1	44	4
	600	94	10	43	21	24	6	5	0
$Ce_{0.8}Gd_{0.2}O_{1.9}$	400	60	6	6	34	1	30	16	13
	600	97	15	21	30	17	15	9	8
$Ce_{0.8}La_{0.2}O_{1.9}$	400	80	7	9	37	2	23	9	20
	600	98	12	29	29	22	14	4	2
$Ce_{0.8}Mg_{0.2}O_{1.8}$	400	69	8	8	35	1	29	10	17
	600	97	14	16	33	15	14	9	13

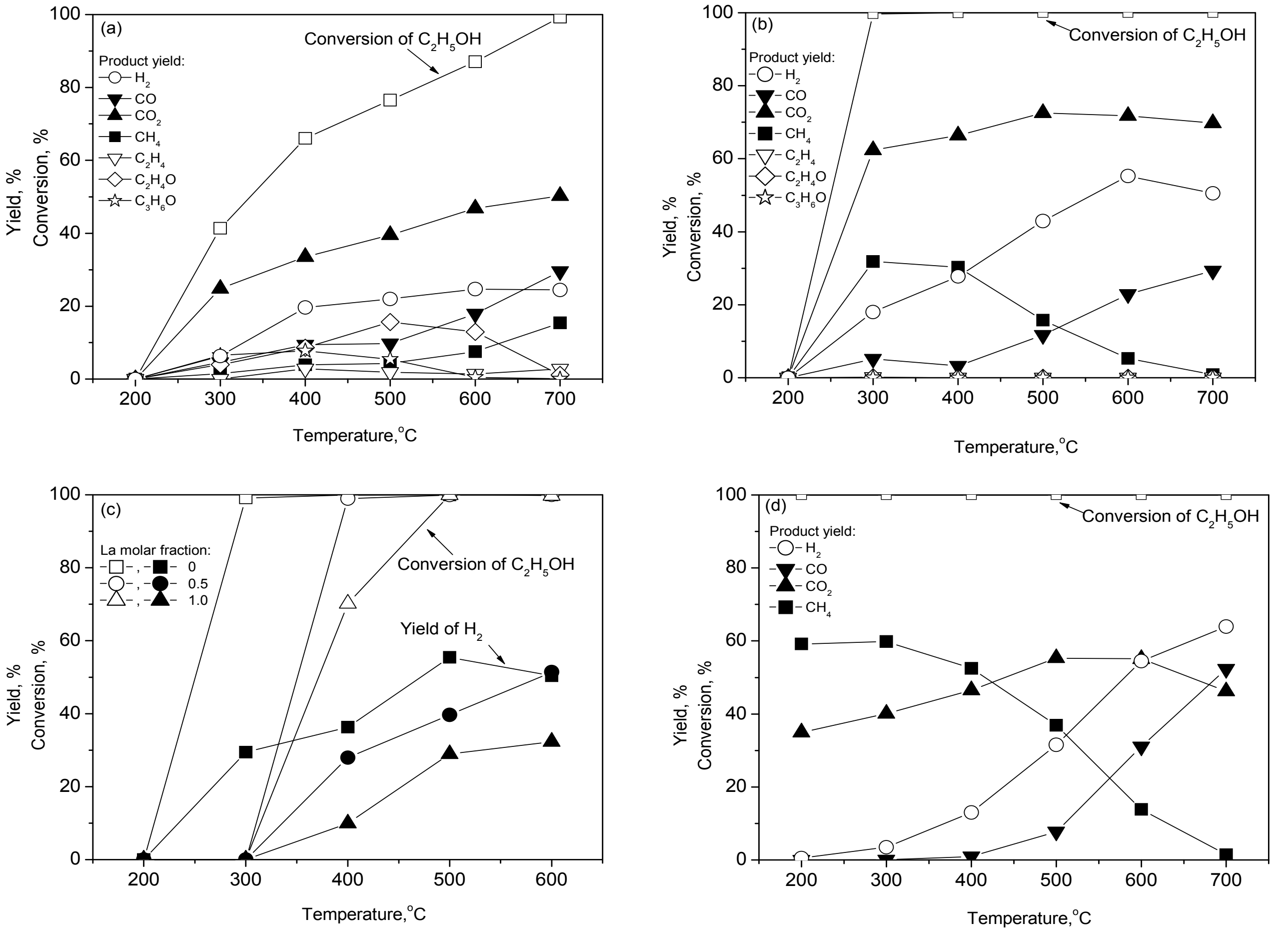

Fig. 3. Conversion of C_2H_5OH and yield of H_2 obtained in the ATR of C_2H_5OH over $2Ni/Ce_{0.8}La_{0.2}O_{1.9}$ (a), $10Ni/Ce_{0.8}La_{0.2}O_{1.9}$ (b), $10Ni/Ce_{1-x}La_xO_y$ (c) and thermodynamic equilibrium values (d).

Table 2

Performance of $Ni/Ce_{1-x}M_xO_y$ catalysts (x = 0, 0.2, 1) in ATR of C_2H_5OH [25]

Sample	T, °C	X_{C2H5OH}, %	Y_{H2}, %	Selectivity, %					
				CO	CO_2	CH_4	C_2H_4	C_2H_4O	C_3H_6O
$10Ni/CeO_2$	400	100	36	5	69	26	0	0	0
	600	100	50	24	71	5	0	0	0
$10Ni/Gd_2O_3$	400	100	17	11	60	29	0	0	0
	600	100	42	42	53	5	0	0	0
$10Ni/La_2O_3$	400	70	10	6	55	1	3	20	0
	600	100	32	19	70	11	0	0	15
10Ni/MgO	400	64	12	15	43	7	0	35	0
	600	93	44	41	49	1	2	7	0
$10Ni/Ce_{0.8}Gd_{0.2}O_{1.9}$	400	79	19	16	44	17	2	21	0
	600	100	46	25	64	11	0	0	0
$10Ni/Ce_{0.8}La_{0.2}O_{1.9}$	400	100	26	4	65	31	0	0	0
	600	100	56	33	64	4	0	0	0
$10Ni/Ce_{0.8}Mg_{0.2}O_{1.8}$	400	65	12	7	48	10	2	31	2
	600	100	40	23	69	8	0	0	0

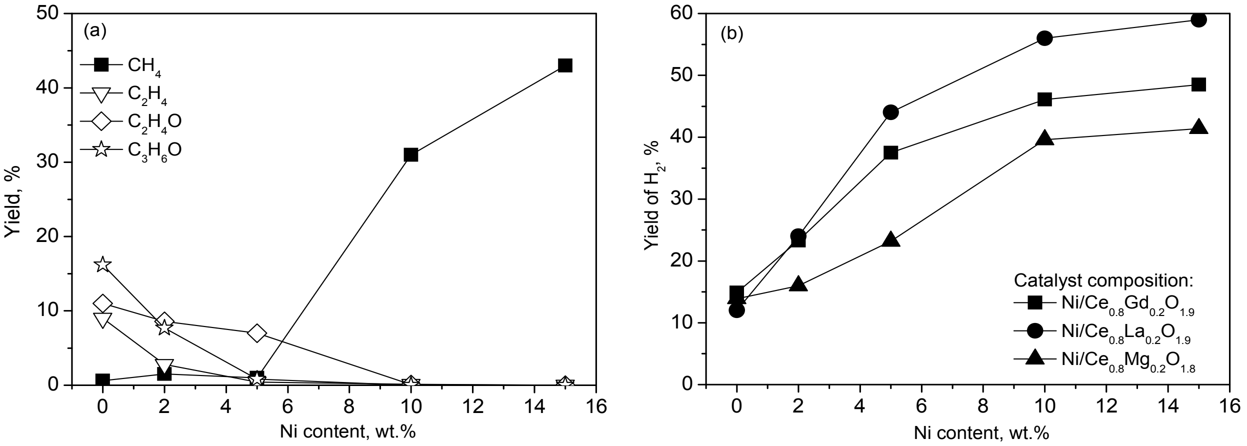

Fig. 4. Dependence of yield of products obtained in the ATR of C_2H_5OH over $Ni/Ce_{0.8}La_{0.2}O_{1.9}$ (a) and $Ni/Ce_{0.8}M_{0.2}O_{1.9}$ (b) catalysts on Ni content. Reaction temperature – 300 °C (a), 600 °C (b).

It is noted that in this case, the high yield of methane is already observed at low values of reaction temperature and it decreases with a growth of reaction temperature (Fig. 3b). Dependence of Y_{CH4} and Y_{CO} vs. temperature shows the increase of contribution of methane steam reforming reaction with increasing of reaction temperature. The comparison of the obtained product yields over the 10Ni catalyst (Fig. 3b) with thermodynamic equilibrium yields (Fig. 3d) shows that these values are close to each other. On the contrary, at low Ni content the significant deviation is observed (Fig. 3a, Fig. 3d). It means that in this case the reaction studied is far from the equilibrium state and it is controlled by kinetic limitations.

The increase of Ni content also leads to a decrease in the temperature of complete ethanol conversion and an increase of hydrogen yield (Fig. 3, Fig. 4b). In particular, over $Ni/Ce_{0.8}La_{0.2}O_{1.9}$ catalyst upon the increase of Ni content from 2 to 15 wt.% X_{C2H5OH} decreases from 700 to 300 °C (Fig. 3) while Y_{H2} at 600 °C grows from 15 to 60% (Fig. 4b). The performance of samples with 10 and 15 wt.% Ni is comparable and 10 wt.% Ni may be regarded as appropriate content for high catalyst performance in the studied reaction. In general, the optimal Ni content depends on support composition and reaction conditions. For example, the 30 wt.% Ni is selected as the optimal value for Ni/CeO_2-ZrO_2 catalysts for steam reforming of C_2H_5OH [31]. It can be seen (Fig. 4b) that the best hydrogen yield in ATR of C_2H_5OH is achieved in the presence of Ni catalysts on the basis of $Ce_{0.8}La_{0.2}O_{1.9}$ support while the least activity was shown by the catalysts based on $Ce_{0.8}Mg_{0.2}O_{1.8}$ support. As was shown in Part 1 of this article, these $10Ni/Ce_{0.8}M_{0.2}O_y$ samples have a similar average size of NiO particles but different ability in reduction that consequently can affect the catalyst performance (Fig. 4b).

At high Ni content (10–15 wt.%) the features of the supports own activity in the reaction is mainly exhibited by catalysts on the individual oxides while the performance of catalysts on mixed oxides differs more strongly at $T_{reaction} < 450$ °C (Table 2). In this case, dopant type and content have the impact on the catalyst performance mainly through the regulation of active component properties. The optimal value of the dopant content in support composition depends on the kind of dopant (Fig. 5). For example, with a decrease of a molar fraction of lanthanum in the support, the dependence (Y_{H2} vs. $T_{reaction}$) removes to lower temperatures, and the yield of hydrogen increases (Fig. 3c, Table 3). This correlates with a deterioration of nickel dispersion and improvement of reducibility of nickel cations (Part 1 of this article). It is in agreement with findings in earlier works [31–33]. Different oxygen storage capacity of supports also may have an impact on catalyst performance [13, 31].

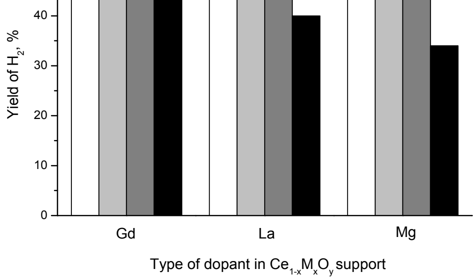

Fig. 5. Yield of H_2 in the ATR of C_2H_5OH at 600 °C over $Ni/Ce_{1-x}Gd_xO_y$, $Ni/Ce_{1-x}La_xOy$ and $Ni/Ce_{1-x}Mg_xO_y$ catalysts.

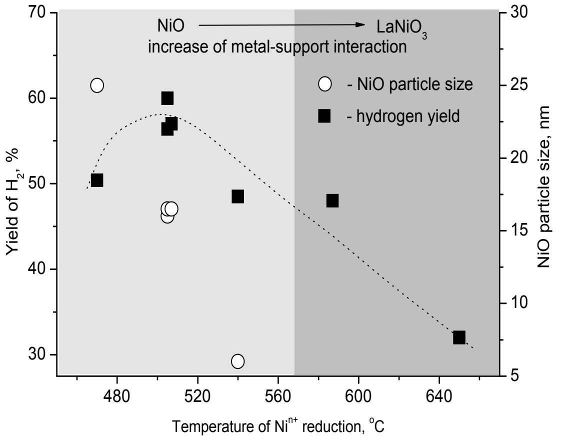

Fig. 6. Yield of H_2 in ATR of C_2H_5OH over $10Ni/Ce_{1-x}La_xO_y$ catalysts versus its structural and redox characteristics.

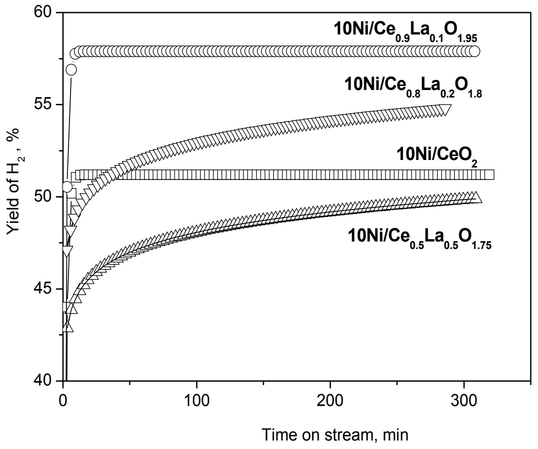

Fig. 7. Yield of H_2 in the ATR of C_2H_5OH over $10Ni/Ce_{1-x}La_xO_y$ catalysts versus time on stream at 600 °C.

Table 3

Effect of La molar fraction on performance of $10Ni/Ce_{1-x}La_xO_y$ catalysts in ATR of C_2H_5OH at 600 °C

$Ni/Ce_{1-x}La_xO_y$	X_{C2H50H}	Y_{H2}	Y_{CO}	Y_{CO2}	Y_{CH4}
x = 0	100	50	24	71	5
x = 0.1	100	56	45	54	1
x = 0.2	100	56	33	64	4
x = 0.5	100	51	32	66	1
x = 0.8	100	48	23	66	11
x = 0.9	100	40	20	69	11
x = 1	100	32	19	70	11

Figure 6 shows the dependence of H_2 yield in ATR of C_2H_5OH over $10Ni/Ce_{1-x}La_xO_y$ catalysts on its structural and redox characteristics. The variation of La content in $Ce_{1-x}La_xO_y$ affects the mode of interaction between Ni supported species and $Ce_{1-x}La_xO_y$ support. In particular, the intensification of such interaction appears as change in phase composition and dispersion of Ni active component as well as its $T_{reduction}$: at x = 0–0.2 → NiO (13–25 nm) → T = 470–500 °C, at x = 0.5–0.8 → NiO (< 8 nm) → T= 540–580 °C and at x = 0.9–1 → $LaNiO_3$ → T = 650 °C. It turns out that an increase in the degree of interaction between the components of the catalyst has both positive (improvement of the dispersion and anti-sintering ability) and negative (decrease of the ability to reduction and, accordingly, the concentration of Ni^o active centers) effects [28, 31, 34]. In this connection, a volcano-type dependence of the hydrogen yield on the degree of interaction between metal and support is observed. It is reported [35] that both the moderate metal-support interaction and the right ability to be reduced contribute to the high performance of $Ni/Mg_{0.75}Ti_{0.25}O$ and $Ni/Mg_{0.5}Ti_{0.5}O$ catalysts in tri-reforming of methane. So, the yield of H_2 can be maximized through optimization of support composition which will provide the necessary for this system mode of the interaction of the catalytically active species with the support matrix.

The developed catalyst shows the stable characteristics in the studied catalytic process (Fig. 7). It is noted that these experiments were conducted without pre-reduction of catalysts. The data of Fig. 7 indicates that catalysts are capable of self-activation. The samples are reduced under reaction mixture that provides the formation of Ni^o active sites. The decrease of reducibility of Ni^{n+} cations in $10Ni/Ce_{1-x}La_xO_y$ in comparison to those in $10Ni/CeO_2$ leads to the appearance of an induction period of the reaction.

According to [32, 36–38], Y_{H2} (mol of H_2/mol of ethanol) in ATR of C_2H_5OH can be equal to 2.1–4.5. In the presence of our catalyst the value of 3.5 mol of H_2/mol of ethanol is attained. At 600 °C on $10Ni/Ce_{0.8}La_{0.2}O_{1.9}$ catalyst the H_2 yield of 50% was achieved at C_2H_5OH conversion of 100%. Stable and high performance of developed catalysts in ATR of C_2H_5OH indicates the promise of their use in the production of hydrogen.

4. Conclusions

Nickel catalysts on $Ce_{1-x}M_xO_y$ supports were prepared and their catalytic properties in ATR of C_2H_5OH were studied against Ni content (0–15 wt.%) and composition of $Ce_{1-x}M_xO_y$ support

(M = Gd, La, Mg). Irrespectively of support composition, the increase of Ni content up to 10–15 wt.% provides an increase of H_2 yield and a decrease of C_2-C_3–products yield. At a low nickel content, support composition determines the selectivity of by-products formation, especially in the low-temperature region. The growth of H_2 yield in ATR of C_2H_5OH over Ni/$Ce_{1-x}M_xO_y$ catalysts is observed in the next series of supports: $Ce_{1-x}Mg_xO_y$ < $Ce_{1-x}Gd_xO_y$ < $Ce_{1-x}La_xO_y$ or with a decrease of the molar fraction of a dopant up to an optimal value that correlates with the enhancement of the active component reducibility.

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