UDC 544.478.1

DOI: 10.15372/CSD2020246

Development of Supported Ni Catalysts for Autothermal Reforming of Methane

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(Received December 25, 2019; revised May 31, 2020)

Abstract

Nickel catalysts supported on modified alumina were synthesised, their physicochemical properties and activity in the reaction of autothermal reforming of methane (ATR CH_4) were studied. Regulation of physicochemical and, consequently, functional properties of the samples was performed by the modification of ($\gamma + \delta$)-Al_2O_3 support with the additives of different composition $Ce_{1-x}M_xO_y$ (M = Gd, La, Mg; x = 0, 0.2, 0.5, 0.8 и 1; $1 \le y \le 2$) in the amount of 10 mass %. It is shown that $Ni/Ce_{1-x}M_xO_y/Al_2O_3$ are mesoporous materials with specific surface area 80±5 m^2/g, slightly changing with the variations of the composition of modifying additive. The phases of alumina ($\gamma + \delta$)-Al_2O_3), fluorite-like solid solution based on CeO_2 with an average crystallite size 9.0±1.5 nm and nickel oxide NiO are present in the catalysts. The average size of NiO particles is varied in the range from 6.0 to 13.5 nm and is determined by the composition of modifying additive, decreasing with an increase of x, and in the following sequence of oxide additives: $CeO_2 > MgO > Gd_2O_3 > La_2O_3$. The catalysts are capable of self-activation under the ATR CH_4 reaction conditions, and this effect is enhanced in the following row of M: Mg < Gd < La, which is in good correlation with the reducibility of samples. The optimal catalyst $Ni/Ce_{0.5}La_{0.5}O_{1.75}/Al_2O_3$ is revealed, providing the hydrogen yield of 80 % upon 100 % methane conversion at 850 °C. The use of the developed catalysts for the energy-effective conversion of natural and associated petroleum gases into the hydrogen-containing gas is promising.

Keywords: Ni catalyst, support modification, autothermal reforming, methane

INTRODUCTION

Natural gas (NG) and associated petroleum gas (APG), similarly to the new kinds of gas hydrocarbon raw materials – coalmine methane and biogas, serve as valuable resources for the production of various chemical products [1–4]. It is known that oil production is accompanied by the evolution of APG (several thousand m^3 per 1 t of oil). The major components of APG are methane (67–92 %) and ethane (2–14 %), which makes this gas an essential raw material for the chemical industry. For a long time, the major method of APG utilization was its combustion at the production site, which caused non-recoverable losses of the valuable hydrocarbon resource. In addition, the emission of enormous amounts of CO_2, dust, soot and toxic substances accompanying combustion causes environmental pollution and is a reason for substantial ecological problems. One of the examples in the Severnyi District of the Novosibirsk Region, with its seven oil deposits (Verkh-Tarskoye, Maloichskoye, Vostochno-Tarskoye, Tay-Dasskoye, Rakitinskoye, Vostochnoye and Vostochno-Mezhovskoye) and one gas condensate deposit – Veselovskoye. Total gas resources are about 2.9 billion m^3, the proved oil resources are about 47 million t, and predicted resources are estimated 111 million t. The Novosibirsk Region holds the third position in Siberia next to the Tyumen and Tomsk Regions in the amounts of produced and realized oil. The modern level of oil production is about 400 thousand t per year.

In addition to meeting the requirements of environmental legislation, another essential aspect of the successful development of oil and gas industry is the necessity of passing from the present raw export model of economic development to the innovation high-technological model [3]. The resource innovative model of development implies deep hydrocarbon processing, obtaining and export of readily marketable products (for example, hydrogen and ethylene), as their cost is substantially higher than the cost of initial raw material. In general, resource-saving processing of gas raw resources should give additional amounts of commercial products, enhance the efficiency of the oil and gas industry and improve the ecological situation in regions rich in natural resources. Therefore, for the purpose of providing ecologically safe and reasonable nature management, it is necessary to decrease the amount of APG burnt and to process NG and APG into valuable necessary products and semi-products of the chemical industry. A fruitful approach to solving this problem may become the development of new catalytic processes and improvement of the ones for the reasonable treatment of hydrocarbon resources.

Reforming of hydrocarbon resources is the major method of obtaining hydrogen-containing gas. Authothermal reforming (ATR) combines the endothermic steam reforming process

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H^0_{298K} = +206 \text{ kJ/mol} \qquad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^0_{298K} = -41 \text{ kJ/mol} \qquad (2)$$

and exothermal oxidation reactions

$$CH_4 + 1/2O_2 \leftrightarrow CO + 2H_2 \quad \Delta H^0_{298K} = -36 \text{ kJ/mol} \qquad (3)$$

$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O \quad \Delta H^0_{298K} = -802 \text{ kJ/mol} \qquad (4)$$

by feeding the fuel, for example, methane (CH_4), oxygen (or air) and water into the reactor simultaneously, so that exothermal oxidation (3, 4) supplies energy to endothermal steam reforming (1, 2).

Autothermal reforming may proceed within broad ranges of temperature (800–1000 °C) and pressure (0.1–10 MPa), as well as the composition of raw material and steam/hydrocarbon ratio [5]. The thermal effect of the process, similarly to the H_2/CO ratio in the resulting synthesis gas (H_2 + CO), may be regulated by changing the steam/carbon or oxygen/carbon in the initial mixture:

$$CH_4 + z/2O_2 + (1 - z)H_2O \leftrightarrow CO + (3 - z)H_2 \quad \Delta H^0_{298K} = (206.2 - 241.8z) \text{ kJ/mol} \qquad (5)$$

A catalyst for ATR should possess high thermal stability. This requirement is met by nickel catalysts supported on aluminium oxide. An efficient method of improving the functional characteristics of the catalysts is the introduction of modifying additives. The introduction of the additive into the support causes changes in the nature of metal-support interaction. This is a key factor determining the properties of supported metal-containing particles [6–8]. In particular, the chemical composition of the support may affect the size, morphology, electron and oxidation-reduction properties of supported metal particles and thus their catalytic properties. It was established [9] that the catalyst 6 % Co/Al_2O_3 exhibits low activity in the partial oxidation of methane and is rapidly deactivated. The introduction of CaO into the support provides an increase in sample activity due to the improvement and the ability of Co_3O_4 to recover into metal Co^0, which is active in the reaction. In addition, the rate of catalyst carbonization decreases, a decrease in the size of metal cobalt particles and deceleration of the formation of inactive spinel phase $CoAl_2O_4$ are observed. It was demonstrated [10, 11] that the introduction of CeO_2 and La_2O_3 improves the catalytic properties of Ni/Al_2O_3 in the ATR of CH_4 by preventing strong interaction between NiO and Al_2O_3 with the formation of the $NiAl_2O_4$ phase, which promotes the formation of the active Ni^0 phase at the stage of catalyst activation. A positive role of the addition of MgO into the Ni/Al_2O_3 catalyst was reported [12], which is connected with the implementation of the strong interaction between the metal and the support. After catalyst activation in hydrogen, this leads to the formation of fine active Ni^0 particles that are stable against agglomeration and carbonization.

The efficiency of the participation of the support in the catalytic process is determined by the presence of functional groups, the oxygen capacity of the material and the mobility of oxygen in the support matrix. Special attention is attracted by mixed oxides based on cerium dioxide, which are characterized by unique oxidation-reduction properties. It was established [13] that the presence of $CeZrO_2$ in the support causes a decrease in the rate of formation of carbon deposits because it provides an additional route for the adsorption and dissociation of O_2 and H_2O with the formation of active oxygen forms entering the oxidation of carbon-containing intermediates to CO or CO_2. In this connection, it is proposed in the work to use mixed oxides $Ce_{1-x}M_xO_y$ (M = Gd, La, Mg; molar fraction x = 0, 0.2, 0.5, 0.8 и 1; $1 \leq y \leq 2$) as modifying agents.

The present work is a continuation of our studies into the development of approaches to governing the functional properties of materials through the directed regulation of their physicochemical characteristics, development of efficient catalysts for the conversion of NG and APG into hydrogen-containing gas [14–19] and deals with the studies of the effect of the composition of modifying additives $Ce_{1-x}M_xO_y$ on the physicochemical properties of Ni/Al_2O_3 catalysts and their activity in the ATR of CH_4.

EXPERIMENTAL

Procedures for the synthesis of supports and catalysts

The synthesis of modified supports $Ce_{1-x}M_xO_y/Al_2O_3$ was carried out by the joint incipient wetness impregnation of the initial support $(\gamma + \delta)$-Al_2O_3 with the aqueous solution of a mixture of metal salts (cerium nitrate hexahydrate $Ce(NO_3)_3 \cdot 6H_2O$, gadolinium nitrate hexahydrate $Gd(NO_3)_3 \cdot 6H_2O$, lanthanum nitrate hexahydrate $La(NO_3)_3 \cdot 6H_2O$, magnesium nitrate hexahydrate $Mg(NO_3)_2 \cdot 6H_2O$) in the required concentrations. Then the samples were dried under the IR lamp and calcined in a muffle furnace at 850 °C for 6 h. The content of the modifying additive $Ce_{1-x}M_xO_y$ in the supports was 10 mass %.

For the synthesis of catalysts, the modified supports were subjected to incipient wetness impregnation with the aqueous solution of nickel salt (nickel nitrate hexahydrate $Ni(NO_3)_2 \cdot 6H_2O$), then dried under the IR lamp and annealed in the muffle furnace at 500 °C for 4 h. Nickel content in the resulting catalysts was 10 mass %.

Physicochemical methods of investigation

Metal content in the samples under investigation was determined using the X-ray spectral fluorescence method with the help of an ARL ADVANT'X analyzer (ThermoTechno Scientific, Switzerland) with an Rh-anode of the X-ray tube.

The texture characteristics of the catalysts, namely specific surface area (S_{BET}), pore volume (V_Σ) and the average diameter of pores (D_{por}), were investigated using an automatic volumetric set-up ASAP 2400 (Micromeritics, USA) by measuring and processing the isotherms of the low-temperature adsorption of nitrogen at 77 K.

X-ray diffraction (XRD) studies of the samples were carried out with the help of an HZG-4C diffractometer (Freiberger Prazisionmechani, Germany) using monochromatic CoK_α-radiation (λ = 1.79021 Å). The phase composition was determined from the diffraction patterns obtained by scanning the angle region 2θ = 10–85 deg, with a step of 0.1 deg and accumulation time 6–15 s. Since the lines of the phases of initial support $(\gamma + \delta)$-Al_2O_3 appear in the close angle regions and are superimposed on each other, the description was made using the formal cell parameter (a, Å) of aluminium oxide [19], determined from the (440) line with the accuracy of ±0.005 Å. The coherent length (CL) was calculated from the broadening of the diffraction peaks of detected phases according to the Selyakov-Scherrer procedure.

Procedure to investigate the activity of catalysts in the ATR of CH_4

Investigation of the activity of catalysts in the ATR of CH_4 was carried out in a flow quartz reactor (inner diameter 14 mm) within temperature range 300–900 °C at atmospheric pressure, the initial flow rate of the gas mixture was 200 mL/min, and the molar ratio of the reagents was $CH_4/H_2O/O_2/He = 1 : 1 : 0.75 : 2.5$. The tests of samples were carried out purposefully without their preliminary activation in hydrogen. The reaction mixture was analyzed with the help of the mass spectrometric analyzer QMS 300 (Stanford Research Systems, USA), and then the parameters of the process were calculated: concentrations of the substances (vol. %), methane conversion (X_{CH_4}, %), and the yields of hydrogen (Y_{H_2}, %) and CO (Y_{CO}, %) [14].

RESULTS AND DISCUSSION

The results of the studies of textural and structural properties of $Ni/Ce_{1-x}M_xO_y/Al_2O_3$ samples are presented in Table 1.

According to the data of low-temperature nitrogen adsorption, the IV type of adsorption isotherm with the hysteresis loop of H3 type is

TABLE 1

Textural and structural properties of $Ni/Ce_{1-x}M_xO_y/Al_2O_3$ catalysts

Sample	Textural characteristics			XRD data		
	S_{BET}, m^2/g	V_{Σ}, cm^3/g	D_{por}, nm	Phase composition	a, Å	CL, nm
Ni/Al_2O_3	91	0.33	14.6	$(\gamma + \delta)$-Al_2O_3	7.897	–
				NiO	–	10.0
$Ni/CeO_2/Al_2O_3$	77	0.28	14.7	$(\gamma + \delta)$-Al_2O_3	7.893	–
				CeO_2	5.411	13.0
				NiO	–	13.5
$Ni/Ce_{0.8}Gd_{0.2}O_{1.9}/Al_2O_3$	76	0.30	15.7	$(\gamma + \delta)$-Al_2O_3	7.896	–
				CeO_2*	5.419	10.5
				NiO	–	12.5
$Ni/Ce_{0.5}Gd_{0.5}O_{1.75}/Al_2O_3$	–	–	–	$(\gamma + \delta)$-Al_2O_3	7.907	–
				CeO_2*	5.427	10.0
				NiO	–	8.5
$Ni/Ce_{0.2}Gd_{0.8}O_{1.6}/Al_2O_3$	74	0.30	16.0	$(\gamma + \delta)$-Al_2O_3	7.907	–
				CeO_2*	5.424	8.5
				NiO	–	9.0
$Ni/GdO_{1.5}/Al_2O_3$	–	–	–	$(\gamma + \delta)$-Al_2O_3	7.903	–
				F1**	–	–
				NiO	–	8.5
$Ni/Ce_{0.8}La_{0.2}O_{1.9}/Al_2O_3$	76	0.30	15.7	$(\gamma + \delta)$-Al_2O_3	7.899	–
				CeO_2*	5.421	10.0
				NiO	–	11.0
$Ni/Ce_{0.5}La_{0.5}O_{1.75}/Al_2O_3$	–	–	–	$(\gamma + \delta)$-Al_2O_3	7.903	–
				CeO_2*	5.438	9.5
				NiO	–	8.0
$Ni/Ce_{0.2}La_{0.8}O_{1.6}/Al_2O_3$	71	0.29	16.1	$(\gamma + \delta)$-Al_2O_3	7.898	–
				CeO_2*	5.434	9.0
				NiO	–	6.0
$Ni/LaO_{1.5}/Al_2O_3$	72	0.26	14.7	$(\gamma + \delta)$-Al_2O_3	7.903	–
				F2**	–	–
				NiO	–	8.5
$Ni/Ce_{0.8}Mg_{0.2}O_{1.8}/Al_2O_3$	85	0.30	14.7	$(\gamma + \delta)$-Al_2O_3	7.897	–
				CeO_2*	5.413	10.0
				NiO	–	10.0
$Ni/Ce_{0.5}Mg_{0.5}O_{1.5}/Al_2O_3$	–	–	–	$(\gamma + \delta)$-Al_2O_3	7.919	–
				CeO_2*	5.419	10.0
				NiO	–	11.5
$Ni/Ce_{0.2}Mg_{0.8}O_{1.2}/Al_2O_3$	75	0.30	15.9	$(\gamma + \delta)$-Al_2O_3	7.919	–
				CeO_2*	5.414	9.5
				NiO	–	7.5
$Ni/MgO/Al_2O_3$	–	–	–	Al_2O_3***	7.926	–
				NiO	–	11.5

Note. Dash in the table means that the parameter was not determined.

* The phase of fluorite-like solid solution based on CeO_2.

** Traces of non-identified fine phase.

*** The phase of the solid solution based on spinel structure of the low-temperature form of aluminium oxide.

observed for the samples at P/P_0 above 0.7 (Fig. 1), which is evidence of the presence of mesopores [20]. The specific surface area of the $Ni/Ce_{1-x}M_xO_y/Al_2O_3$ catalyst is practically independent of the composition of modifying additive and is equal to 80±5 m^2/g, which is somewhat lower than that for the Ni/Al_2O_3 sample (see Table 1). This may be due to the blockage of the pores of aluminium oxide by the particles of the modifying additive. The specific pore volume of the samples is ~0.30 cm^3/g, and the average pore diameter varies within a narrow range of 14.7–16.1 nm.

It is demonstrated by means of XRD that the catalysts contain the phases related to the support: $(\gamma + \delta)$-Al_2O_3 and a fluorite-like solid solution based on CeO_2 ($Ce_{1-x}M_xO_y$), and the active component (NiO) (see Table 1, Fig. 2). One can see that the formal cell parameter a for aluminium oxide depends on the composition of the modifying additive. A significant increase in parameter a from 7.897 Å (for catalysts based on non-modified support) to 7.919–7.926 Å (for Mg-containing samples) may be the evidence of the interaction of aluminium oxide with the components of the system with the formation of solid solutions based on the spinel structure of the low-temperature form of aluminium oxide.

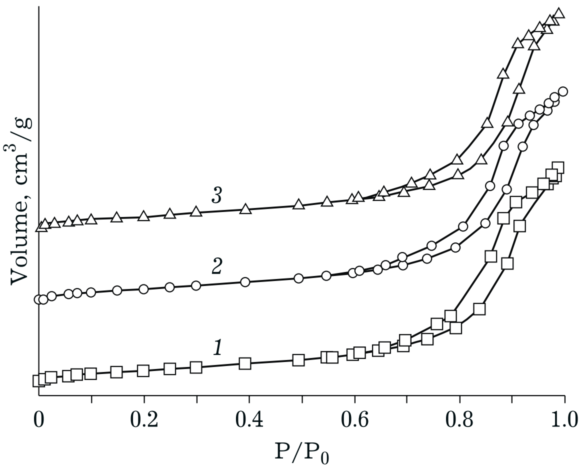

Fig. 1. The isotherms of nitrogen adsorption at 77 K for samples: $Ni/Ce_{0.2}Gd_{0.8}O_{1.6}/Al_2O_3$ (*1*); $Ni/Ce_{0.2}La_{0.8}O_{1.6}/Al_2O_3$ (*2*); $Ni/Ce_{0.2}Mg_{0.8}O_{1.2}/Al_2O_3$ (*3*).

The structural parameters of $Ce_{1-x}M_xO_y$ vary in agreement with the ion radius M (r) and the value of x. For instance, in the case of Gd and La cations with $r(Gd^{3+}) = 0.105$ nm and $r(La^{3+}) = 0.116$ nm, the cell parameter of the solid solution based on CeO_2 increases with an increase in x (see Table 1), which is the evidence of the substitution of cerium cations with $r(Ce^{4+}) = 0.097$ nm by the cations of larger radius. This effect is almost unexpressed for Mg-containing samples in which a decrease in the cell parameter might be expected, taking into account the smaller radius of magnesium cation $r(Mg^{2+}) = 0.072$ nm. In this case, cerium dioxide doping with magnesium cations is likely to proceed not completely. Some magnesium cations, for example in the $Ni/MgO/Al_2O_3$ sample ($x = 1$), can interact with aluminium oxide with the formation of solid solutions Al–Mg–O based on the spinel structure of the low-temperature form of aluminium oxide. It should be also stressed that the CL of CeO_2 decreases from 13 to 9 nm with an increase in the molar fraction of M from 0.2 to 0.8 in the modifying additive (see Table 1). This may be due to the inhibition of crystallite growth because of the presence of the dopant M [21]. The absence (according to XRD data) of the crys-

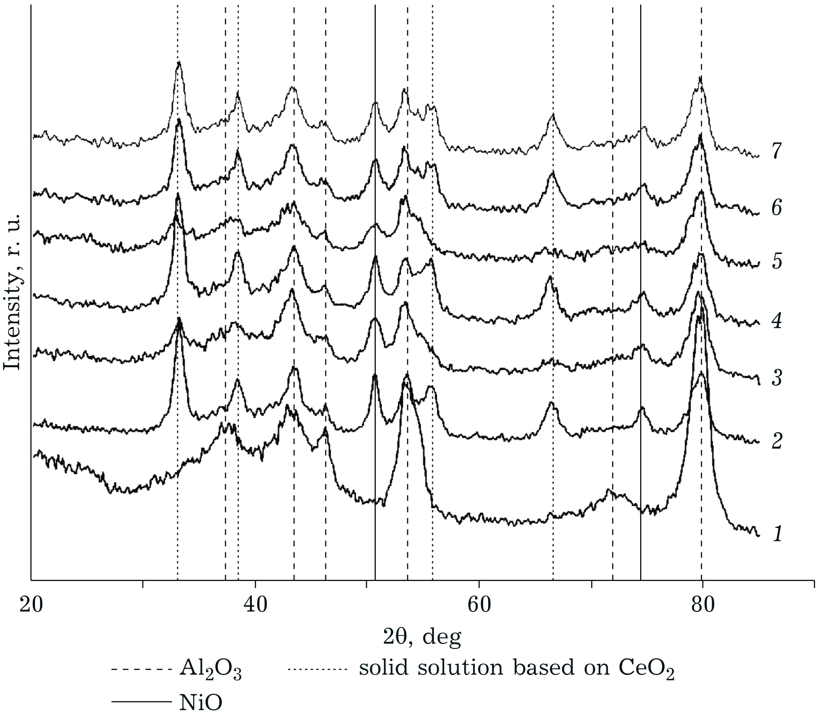

Fig. 2. X-ray diffraction patterns of samples: Al_2O_3 (*1*); $Ni/Ce_{0.8}Gd_{0.2}O_{1.9}/Al_2O_3$ (*2*); $Ni/Ce_{0.2}Gd_{0.8}O_{1.6}/Al_2O_3$ (*3*); $Ni/Ce_{0.8}La_{0.2}O_{1.9}/Al_2O_3$ (*4*); $Ni/Ce_{0.2}La_{0.8}O_{1.6}/Al_2O_3$ (*5*); $Ni/Ce_{0.8}Mg_{0.2}O_{1.8}/Al_2O_3$ (*6*); $Ni/Ce_{0.2}Mg_{0.8}O_{1.2}/Al_2O_3$ (*7*).

tallized phases of individual Gd, La or Mg oxides does not exclude their presence in the sample in the finely dispersed state.

It follows from the analysis of the data shown in Table 1 that the average size of NiO particles varies within the range of 6.0–13.5 nm and is determined by the composition of the modifying additive. A trend is observed to its decrease with an increase in x and also in the sequence of oxides: CeO_2 > MgO > Gd_2O_3 > La_2O_3. The finest state of the active component is achieved in La-containing samples, which is connected with the strong metal-support interaction [14]. According to the thermodynamic calculations and experimental data [22–25], the formation of a broad range of nickel-containing joint phases with the structure of spinel $NiAl_2O_4$, fluorite $Ce_{1-x}Ni_xO_y$, perovskite $LaNiO_3$ or halite (Ni, Mg)O is possible for the multicomponent samples under investigation. The absence of the peaks related to joint phases in the diffraction patterns does not exclude their presence in the fine state. Indeed, it was shown by means of transmission electron microscope [19] that for NiPd-containing catalysts supported in aluminium oxide modified with various additives (CeO_2, ZrO_2, La_2O_3, $Ce_{0.5}Zr_{0.5}O_2$ and $La_2O_3/Ce_{0.5}Zr_{0.5}O_2$), in addition to NiO particles, there are plate-like $NiAl_2O_4$ ~10 nm in size on the surface of the support. The formation of a mixed solid solution Ni–La–Al–O was also established for La-containing samples.

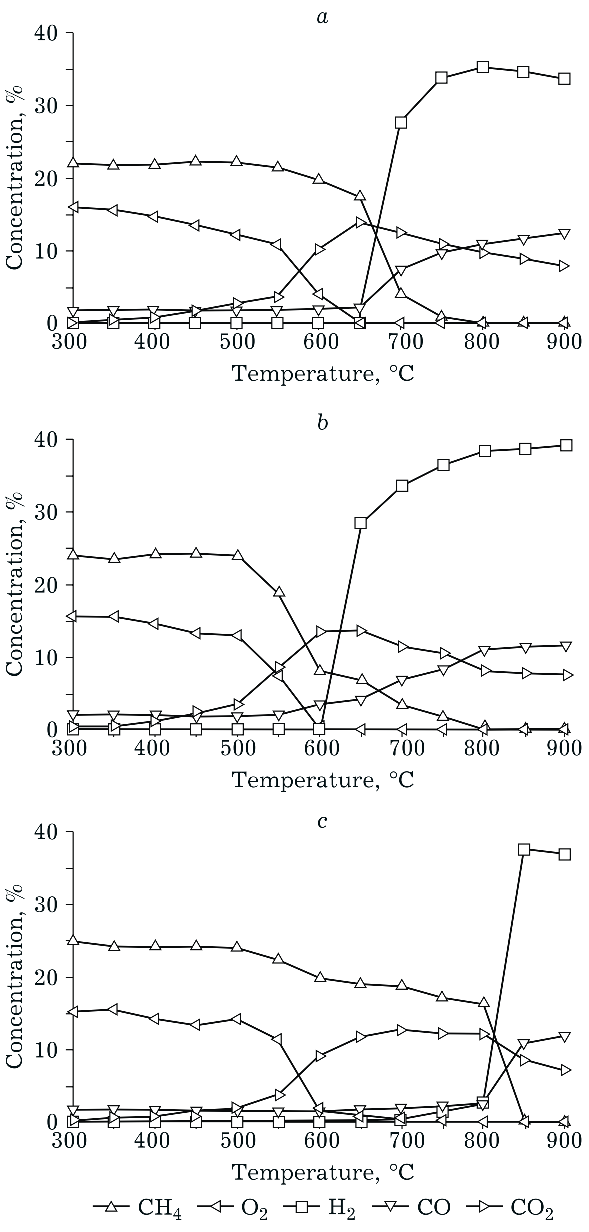

Fig. 3. Temperature dependence of the concentrations of reagents (CH_4, O_2) and products (H_2, CO, CO_2) of the reaction of autothermal reforming of CH_4 in the presence of catalysts $Ni/Ce_{0.5}Gd_{0.5}O_{1.75}/Al_2O_3$ (*a*), $Ni/Ce_{0.5}La_{0.5}O_{1.75}/Al_2O_3$ (*b*) and $Ni/Ce_{0.5}Mg_{0.5}O_{1.5}/Al_2O_3$ (*c*).

As mentioned above, the tests of the samples in the ATR of CH_4 were carried out without preliminary activation of the catalysts in hydrogen. The production of hydrogen through reforming for fuel elements puts forward special requirements to the functional characteristics of the catalysts [26–28]. In particular, the catalysts should be adapted to work in the mode of the everyday run and stop, therefore, they should not require special activation before use. In this cyclic mode of operation, the reduction of nickel cations to the metal state should proceed under the action of the reaction medium.

The temperature dependence of the concentrations of reagents and products of the ATR of CH_4 in the presence of catalysts $Ni/Ce_{1-x}M_xO_y/Al_2O_3$ of different compositions is shown in Fig. 3. The behavior of the dependence of product distribution on reaction temperature is determined by the composition of the modifying additive. In the case of $Ni/Ce_{0.5}Gd_{0.5}O_{1.75}/Al_2O_3$, the conversion of CH_4 in the low-temperature reaction region (T < 600 °C) is insignificant and accounts for 10–15 %. The major reaction is the complete oxidation of methane with the formation of CO_2 and H_2O. The formation of reforming products (H_2 and CO) is observed only starting from 700 °C. The concentrations of H_2 and CO increase with temperature rise, and at a temperature within 800–900 °C they become equal to ~34 and 12 %, respectively (see Fig. 3, *a*). The situation is somewhat changed in the presence of $Ni/Ce_{0.5}La_{0.5}O_{1.75}/Al_2O_3$ catalyst: the formation of reforming products starts at a lower temperature (see Fig. 3, *b*). In

TABLE 2

Activity of $Ni/Ce_{1-x}M_xO_y/Al_2O_3$ catalysts in autothermal reforming of CH_4 at 850 °C (reaction time 6 h)

Sample	X_{CH_4}, %	X_{O_2}, %	Y_{H_2}, %	Y_{CO}, %	H_2/CO
Ni/Al_2O_3	44	99	2	4	0.5
$Ni/CeO_2/Al_2O_3$	100	100	77	56	3.7
$Ni/Ce_{0.8}Gd_{0.2}O_{1.9}/Al_2O_3$	100	100	79	64	3.4
$Ni/Ce_{0.5}Gd_{0.5}O_{1.75}/Al_2O_3$	100	100	65	59	2.9
$Ni/Ce_{0.2}Gd_{0.8}O_{1.6}/Al_2O_3$	99	100	72	60	3.2
$Ni/GdO_{1.5}/Al_2O_3$	99	100	57	57	2.6
$Ni/Ce_{0.8}La_{0.2}O_{1.9}/Al_2O_3$	100	100	76	67	3.0
$Ni/Ce_{0.5}La_{0.5}O_{1.75}/Al_2O_3$	100	100	80	65	3.4
$Ni/Ce_{0.2}La_{0.8}O_{1.6}/Al_2O_3$	100	100	75	64	3.2
$Ni/LaO_{1.5}/Al_2O_3$	98	100	72	55	3.4
$Ni/Ce_{0.8}Mg_{0.2}O_{1.8}/Al_2O_3$	100	100	71	46	4.1
$Ni/Ce_{0.5}Mg_{0.5}O_{1.5}/Al_2O_3$	100	100	67	52	3.5
$Ni/Ce_{0.2}Mg_{0.8}O_{1.2}/Al_2O_3$	98	98	66	53	3.3
$Ni/MgO/Al_2O_3$	40	98	4	16	0.6

addition, the high concentration of H_2 is achieved: 39 %. Lower process parameters are observed in the presence of the $Ni/Ce_{0.5}Mg_{0.5}O_{1.5}/Al_2O_3$ sample (see Fig. 3, *c*). One can see that the process dominating within a broad temperature range is the complete oxidation of methane. The formation of reforming products is observed only at a temperature higher than 800 °C. So, in the sequence of supports $Ce_{1-x}Mg_xO_y/Al_2O_3 > Ce_{1-x}Gd_xO_y/Al_2O_3 > Ce_{1-x}La_xO_y/Al_2O_3$ the temperature of the start of reforming reaction decreases: $850 > 700 > 650$ °C.

These results provide evidence that the developed catalysts possess different abilities to undergo self-activation under the conditions of the ATR of methane. This effect depends on the composition of the support $Ce_{1-x}M_xO_y/Al_2O_3$ and increases as the following sequence of M: Mg < Gd < La. With comparable textural and structural characteristics of the samples under investigation (see Table 1), their oxidation-reduction properties are of decisive importance. It was demonstrated by us previously [14] that the temperature of the reduction of nickel cations decreases in the sequence of supports: Mg- > Gd- > La-containing materials. Correspondingly, an increase in the ability of Ni-containing catalysts to get self-activated is in good correlation with the ability of the catalyst to get reduced [14].

It is known that the composition of the oxide matrix affects both the properties of the active component and on the nature of support participation in the catalytic process. The addition of $Ce_{1-x}M_xO_y$ has a positive effect on the activity of the Ni/Al_2O_3 catalyst in the ATR of CH_4: 1) the catalyst becomes able to get self-activated due to the improvement of reducibility because of a decrease in the degree of the metal-support interaction; 2) Ce-containing systems are characterized by the presence of the centres of H_2O/O_2 activation and are the sources of active oxygen, which participates in the oxidation of carbon (C) at the metal–support interface. Carbon oxidation is accompanied by the removal of oxygen atoms with the formation of oxygen vacancies ($Vo^{\bullet\bullet}$) and, as a consequence, by a decrease in the efficient degree of cerium oxidation:

$$4Ce^{4+} + O^{2-} \leftrightarrow 2Ce^{4+} + 2Ce^{3+} + Vo^{\bullet\bullet} + 0.5O_2$$

$$Ni\text{–}C + 2CeO_2 \rightarrow Ni + CO + Ce_2O_3$$

$$H_2O + Ce_2O_3 \rightarrow 2CeO_2 + H_2$$

A comparison of methane conversion values and hydrogen yield showed (Table 2, Fig. 4) that the most efficient catalyst for the ATR of CH_4 is $Ni/Ce_{0.5}La_{0.5}O_{1.75}/Al_2O_3$: in its presence, the yield of hydrogen at 850 °C is equal to 80 % with the 100 % conversion of methane. The achieved process parameters are close to the equilibrium values [29], are comparable to or higher than the values reported in the literature [10, 13, 30].

CONCLUSION

By means of incipient wetness impregnation, a series of nickel catalysts $Ni/Ce_{1-x}M_xO_y/Al_2O_3$ were synthesized with the variation of the composition of modifying additive (M = Gd, La, Mg; $x = 0$, 0.2, 0.5, 0.8 и 1; $1 \le y \le 2$). A comparative analysis of the textural and structural properties

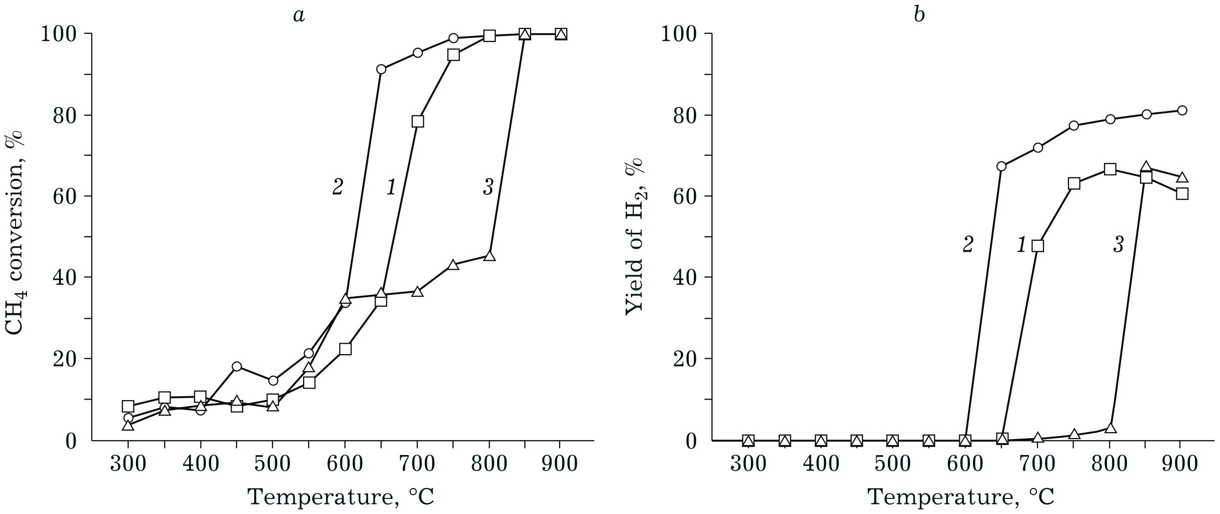

Fig. 4. Temperature dependences of methane conversion (*a*) and hydrogen yield (*b*) in the autothermal reforming of CH_4 in the presence of catalysts $Ni/Ce_{0.5}Gd_{0.5}O_{1.75}/Al_2O_3$ (*1*), $Ni/Ce_{0.5}La_{0.5}O_{1.75}/Al_2O_3$ (*2*) and $Ni/Ce_{0.5}Mg_{0.5}O_{1.5}/Al_2O_3$ (*3*).

of the samples was carried out with the help of physicochemical methods of investigation. It was revealed that the modifying additive is a fluorite-like solid solution based on CeO_2 with the average crystallite size 9.0±1.5 nm. The composition of the modifying additive has no substantial effect on the texture properties of the catalysts, but it determines the disperse state of the active component stabilized mainly in the form of NiO with the average particle size varying within the range 6–13 nm. The average size of NiO particles decreases with an increase in x in the modifying additive $Ce_{1-x}M_xO_y$, as well as in the sequence of oxides: $CeO_2 > MgO > Gd_2O_3 > La_2O_3$. The catalysts exhibit high activity in the ATR of CH_4 without preliminary activation in a reducing medium. The ability to self-activation under reaction conditions increases in the sequence of M: Mg < Gd < La, which is due to the improvement of sample reducibility. The most efficient catalyst was determined: $Ni/Ce_{0.5}La_{0.5}O_{1.75}/Al_2O_3$, in its presence the yield of hydrogen at 850 °C is equal to 80 % with 100 % methane conversion. The application of the catalysts of $Ni/Ce_{1-x}M_xO_y/Al_2O_3$ series in the development of the technology of natural gas and associated petroleum gas processing may allow one to obtain valuable chemical products and to improve the ecological situation, first of all in the regions rich in natural resources.

Acknowledgements

Authors thank Kraevskaya I. L. and Efimenko T. Ya. For assistance in the studies of the samples with the help of physicochemical methods.

The work was carried out with financial support from the Russian Foundation for Basic Research (Project No. 18-33-00882).

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