

Partial Oxidation of Methane to Synthesis Gas: Novel Catalysts Based on Neodymium–Calcium Cobaltate– Nickelate Complex Oxides

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Abstract—Novel catalysts based on neodymium–calcium cobaltate–nickelate complex oxides for the partial oxidation of methane to synthesis gas have been synthesized and studied using catalyst precursors with the general formula $\text{NdCaCo}_{1-x}\text{Ni}_x\text{O}_n$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$) prepared by the solid state synthesis method. It has been shown that the synthesized samples form a series of solid solutions with a K_2NiF_4 structure at $x \leq 0.8$ or a rhombically distorted K_2NiF_4 structure at $x = 1$. The products of conversion of the resulting precursors in a methane–oxygen mixture at high temperatures have shown high methane conversions and synthesis gas yields. The highest values of these parameters have been achieved in the presence of catalysts synthesized by the reduction of $\text{NdCaCo}_{0.4}\text{Ni}_{0.6}\text{O}_n$ and NdCaNiO_n precursors. The complete replacement of cobalt with nickel has led to an increase in the synthesis gas yield; however, it has been found that the resulting catalyst is prone to carbonization. It has been determined that an optimum nickel to cobalt ratio in the catalyst composition provides the formation of a carbonization-resistant catalyst.

Keywords: synthesis gas, partial oxidation of methane, neodymium–calcium cobaltate–nickelate

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The production of synthesis gas (CO-H_2 mixture) by the partial oxidation of methane (POM) is a promising approach to the conversion of methane-containing gases to petrochemicals. Advantages of POM lie in the fact that this process is exothermic and the composition of the resulting synthesis gas ($\text{H}_2/\text{CO} = 2$) is favorable for use in the synthesis of methanol and hydrocarbons by the Fischer–Tropsch reaction.

Thermodynamic calculations show that the equilibrium of the POM reaction is significantly shifted toward the formation of final products even at 700–800°C; however, in the absence of a catalyst, the process occurs at a considerable rate only at temperatures above 1100°C [1, 2].

Known effective POM catalysts are platinum group metals and metallic cobalt and nickel on oxide supports of various chemical origins [1–6]. These catalysts provide the occurrence of the POM reaction with a high degree of methane conversion and a high selectivity for CO and H_2 even at 800–900°C.

In the presence of nickel-based catalysts, the process can occur at lower temperatures than in the presence of cobalt catalysts; however, nickel catalysts are

prone to the formation of carbon deposits on their surface; these deposits block the active sites of the catalyst. The main method for the preparation of Co- and Ni-based catalysts on oxide supports is the impregnation of a porous support with a solution of cobalt or nickel salts and subsequent drying and thermal decomposition of the salts in a reducing medium; the method provides the formation of metal nanoparticles on the highly developed surface of the oxide support.

Recently, the attention of researchers engaged in the development of POM catalysts has been attracted by an approach based on the synthesis of composites in which the active components (nickel, cobalt) are dispersed in a matrix of various supports, which in turn can affect the POM results. To form active nickel or cobalt particles, it is necessary to subject their oxide precursors to a high-temperature reduction.

A compound whose reduction products provided a high yield of CO and H_2 in the POM reaction is NdCaCoO_4 [7, 8]. Similar to other cobalt-based POM catalysts, the resulting catalyst requires relatively high temperatures for the effective occurrence of the process (930–960°C). It is reasonable to expect a decrease

in these temperatures in the case of replacement of a portion or the entire amount of cobalt in NdCaCoO₄ with nickel.

The aim of this study is to explore the possibility of synthesizing POM catalysts by the complete or partial replacement of cobalt in the NdCaCoO₄ matrix with nickel and analyze the conversion and catalytic properties of the resulting materials in a methane–oxygen mixture that is not diluted with an inert gas.

EXPERIMENTAL

NdCaCo_{1-x}Ni_xO_n ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$) materials were prepared by solid state synthesis. Mixtures of Nd₂O₃, CaCO₃, Co₃O₄, and NiO in ratios corresponding to the cationic composition of the final products were wetted with acetone and ground in a Fritsch Pulverisette 5 planetary mill for 1 h. The resulting powders were heat-treated at 1100°C for 24 h, pelletized, annealed at 1200°C for 10 h, ground, repelletized, and annealed at 1200°C for 20 h. The long-term synthesis procedure was used to achieve the maximum homogeneity of the chemical composition of the precursor.

The phase composition of the resulting materials was studied on a Rigaku MiniFlex 600 diffractometer; the diffraction data were processed using the WinXPOW software package.

The morphology of the catalysts before and after use in POM was studied using a Carl Zeiss NVision 40 scanning electron microscope (SEM) equipped with reflected (InLens) and backscattered electron detectors (ESB) at an accelerating voltage of 7 and 1 kV, respectively, and a magnification of up to 200000×.

The catalytic properties of the samples in the POM reaction were studied in a heated flow-type quartz reactor made in the form of a U-shaped tube with an internal diameter of 5 mm and a thermocouple pocket located between the inlet and outlet tubes of the reactor. A catalyst was placed in the lower part of the reactor; the free volume of the reactor below and above the catalyst was filled with quartz chips to limit the contribution of noncatalytic gas-phase methane conversion processes and more correctly characterize the catalytic properties of the samples. The catalyst loaded into the reactor had a particle size of 0.5–1.0 mm and a weight of 0.2 g. The reactor was fed with a mixture of methane (99.99% purity) and oxygen (99.999% purity), which was not diluted with an inert gas. The CH₄/O₂ ratio was 2; the gas mixture space velocity was 9 L (g h)⁻¹. The POM product composition was analyzed by gas chromatography as described in [7, 8].

RESULTS AND DISCUSSION

Analysis of the phase composition of the products of the solid state synthesis of the catalyst precursors (Fig. 1a) showed that, at $x = 0–0.8$, the formation of

compounds with a K₂NiF₄ structure (space group I4/mmm) is observed.

For the sample containing no cobalt, the formation of rhombically distorted K₂NiF₄ structure is observed. All the nickel-containing samples comprise a small amount of NiO. In addition, the cationic composition of the resulting compounds with a K₂NiF₄ structure changes with an increase in the nickel content in the reaction mixture, as evidenced by a shift of reflections (101) and (103) with an increase in the Ni/Co ratio.

Comparison of the phase composition of the catalysts before and after the catalytic conversions of the methane–oxygen mixture (Fig. 1b) shows that the POM reaction leads to the formation of Nd₂O₃, CaO, and Co₃O₄ in the case of NdCaCoO₄ and also NiO in all other cases. At $x \geq 0.6$, the presence of a metallic phase is also observed; owing to the structural similarity of the respective modifications, the reflections of this phase can be attributed to nickel, cobalt, their mixture, or solid solution. It should be noted that, according to most of the researchers, it is the presence of metal particles on the catalyst surface that is responsible for the activity of nickel- and cobalt-containing POM catalysts [1–8].

Results of the POM tests (see Table 1) show that all the studied materials catalyzed the formation of synthesis gas. For all the samples, an increase in the methane conversion and the synthesis gas selectivity with increasing temperature is observed; however, for samples with different Ni/Co ratios, these parameters increase in somewhat different ways. At 829–860°C, the cobalt-containing samples provide an almost complete oxidation of methane to CO₂, as evidenced by the minimum CO yield at a significant degree of conversion of methane (23–28%) and a CO₂ yield of 18–21%. At the same time, an increase in temperature to 895–900°C leads to a change in the behavior of the processes occurring on the catalyst surface and thereby to a significant increase in the CO and H₂ yields with a respective decrease in the CO₂ yield. This finding suggests that the complete catalytic oxidation of methane is replaced by partial oxidation (POM).

The authors of [9] showed that the NdCaCoO₄ compound with a K₂NiF₄ structure is capable of catalyzing the complete oxidation of methane, whereas the products of the reductive decomposition of NdCaCoO₄ catalyze the POM process [7, 8]. Taking into account these features, a change in the behavior of the methane oxidation processes with increasing temperature is apparently attributed to a vigorous reductive decomposition of the studied complex oxides.

The relatively high CO yield observed at $T < 900^\circ\text{C}$ in the presence of catalysts with a high nickel content ($x \geq 0.4$) shows that the reductive decomposition of the oxide precursors of this compound occurs at significantly lower temperatures than for NdCaCoO₄ and

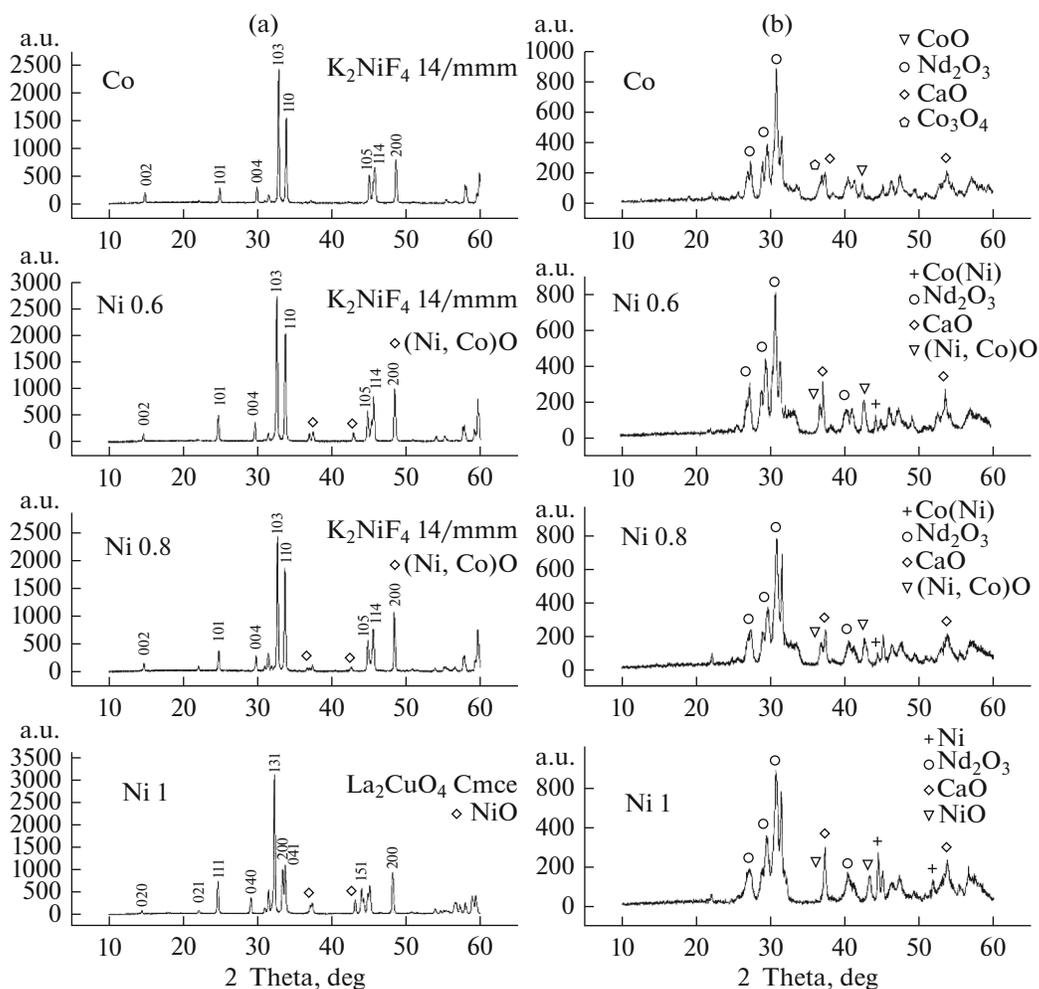


Fig. 1. X-ray diffraction patterns of $\text{NdCaCo}_{1-x}\text{Ni}_x\text{O}_n$ samples with different compositions (a) after synthesis and (b) after catalytic tests.

that catalysts of methane conversion in the entire studied temperature range are the products of their decomposition.

Analysis of the data in Table 1 shows that the variation in the Ni/Co ratio in the precursors and, accordingly, in the products of their thermal reduction has a significant effect on the entire complex of their catalytic characteristics. Thus, for each sample, a temperature providing significant yields of CO and H_2 (more than 20%) was recorded. In the case of NdCaCoO_4 , upon heating to 925°C , the methane conversion was 64% and the CO and H_2 yields were 51 and 54%, respectively; for $\text{NdCaCo}_{0.8}\text{Ni}_{0.2}\text{O}_n$, upon heating to 912°C , the methane conversion was 43% and the CO and H_2 yields were 22 and 41%, respectively. For $\text{NdCaCo}_{0.6}\text{Ni}_{0.4}\text{O}_n$, upon heating to 884°C , at a methane conversion of 45%, the CO and H_2 yields were 28 and 27%, respectively; for $\text{NdCaCo}_{0.4}\text{Ni}_{0.6}\text{O}_n$, at 874°C and a methane conversion of 43%, the CO and H_2 yields were 25% each; for $\text{NdCaCo}_{0.2}\text{Ni}_{0.8}\text{O}_n$, at

931°C and a methane conversion of 55%, the CO and H_2 yields were 39% each; and for NdCaNiO_n , at 832°C , the methane conversion was 78% and the CO and H_2 yields were 68 and 75%, respectively.

Thus, in general, an increase in the nickel content in the catalyst leads to a systematic decrease in temperature providing synthesis gas yields of more than 20%. Noteworthy is the unusual behavior of the catalyst with $x = 0.8$; in the presence of this sample, all the processes occur at higher temperatures than in the presence of the closest counterparts. An explanation to this interesting fact has not yet been found; more detailed further studies in subsequent research are required. At the same time, the catalyst based on the NdCaNiO_n precursor, in which the entire amount of cobalt is replaced with nickel, fully corresponds to the observed tendency. In this case, the formation of synthesis gas is observed even at 787°C ; at 832°C , high methane conversions and CO and H_2 yields are achieved.

Table 1. Results of POM in the presence of catalysts based on $\text{NdCaCo}_{1-x}\text{Ni}_x\text{O}_n$ precursors

$T, ^\circ\text{C}$	CH_4 conversion, %	Yield, %		
		CO	H_2	CO_2
NdCaCoO_4				
829	23	1	0	18
895	26	3	2	19
925	64	51	54	12
972	76	67	74	9
$\text{NdCaCo}_{0.8}\text{Ni}_{0.2}\text{O}_n$				
860	28	0	0	21
912	43	22	41	18
929	66	54	56	12
943	70	59	62	15
962	75	65	68	12
$\text{NdCaCo}_{0.6}\text{Ni}_{0.4}\text{O}_n$				
884	45	28	27	37
934	73	64	66	13
953	78	70	77	11
976	88	83	88	4
$\text{NdCaCo}_{0.4}\text{Ni}_{0.6}\text{O}_n$				
874	43	25	25	17
928	64	52	52	12
968	82	76	83	6
$\text{NdCaCo}_{0.2}\text{Ni}_{0.8}\text{O}_n$				
829	22	0	0	18
900	27	1	0	20
931	55	39	39	15
970	62	49	53	13
NdCaNiO_n				
787	34	13	59	18
832	78	68	75	9
862	81	73	79	8
884	82	75	80	6
920	87	82	88	7
954	93	89	96	3
935	92	88	94	4
902	89	83	92	5

In addition, the data in Table 1 show that, in the set of samples containing both nickel and cobalt, the maximum CO and H_2 yields (83 and 88%, respectively) are provided by $\text{NdCaCo}_{0.6}\text{Ni}_{0.4}\text{O}_n$. The maximum CO and H_2 yields (89 and 96%, respectively) are also observed in the presence of the catalyst based on the NdCaNiO_n precursor. The products of reaction of this sample with a methane–air mixture preserve high synthesis gas selectivity even when the POM tempera-

ture decreases after reaching the highest value. Thus, at 954°C , the CO and H_2 yields are 89 and 96%, respectively; with a decrease in temperature to 935°C , the CO and H_2 yields are 88 and 94%, respectively; at 902°C , these parameters are 83 and 92%, respectively.

As noted above, one of the main problems in the use of POM catalysts based on metallic nickel is the formation of carbon deposits, which lead to a significant decrease in the catalytic activity of these samples.

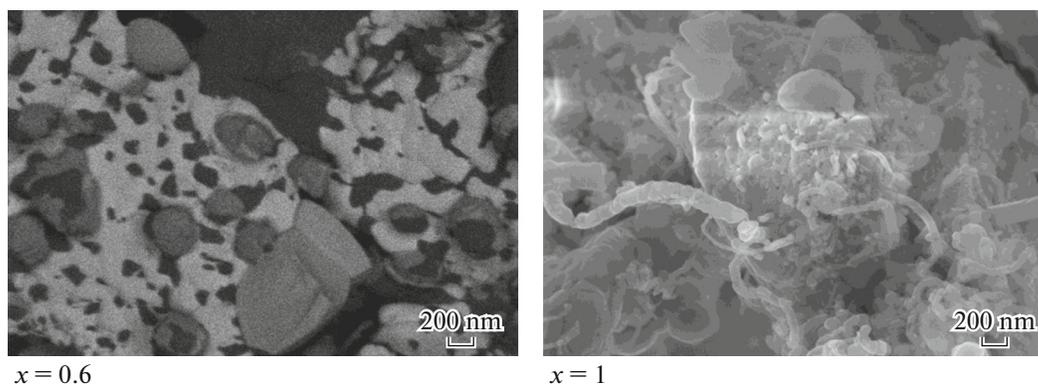


Fig. 2. SEM micrographs of the catalysts based on $\text{NdCaCo}_{1-x}\text{Ni}_x\text{O}_n$ ($x = 0.6$ and 1) precursors after catalytic tests.

During the tests, the catalyst based on the NdCaNiO_n precursor showed stable results for 18 h; however, a further use led to a significant carbonization of the catalyst. SEM studies of the catalysts after POM (Fig. 2) showed that the best of the mixed cobalt–nickel catalysts contained only small fragmentary carbon deposits. At the same time, analysis of the catalyst containing no cobalt confirmed the vigorous formation of carbon fibers with a diameter of up to 200 nm on the surface of the catalyst particles. Taking into account these data, mixed nickel–cobalt catalysts based on the products of conversion of $\text{NdCaCo}_{1-x}\text{NiO}$ under conditions of the POM reaction are apparently of the greatest practical interest.

Thus, the POM reaction in the presence of novel catalysts based on oxide precursors with a general composition of $\text{NdCaCo}_{1-x}\text{Ni}_x\text{O}_n$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$) has been first studied. At $x = 0$, the precursor is the NdCaCoO_4 compound with a K_2NiF_4 structure. At $x \geq 0.2$, the main component of the precursor is a solid solution with a K_2NiF_4 structure; NiO is present as an impurity. It has been shown that the oxide and metal oxide composites resulting from the conversion of the precursors in a flow of a methane–oxygen mixture at high temperatures provide high methane conversions and CO and H_2 yields in the POM reaction. Maximum values of these parameters are achieved in the presence of catalysts synthesized by the reduction of $\text{NdCaCo}_{0.4}\text{Ni}_{0.6}\text{O}_n$ and NdCaNiO_n precursors. The complete replacement of cobalt with nickel leads to an improvement of the POM parameters; however, it is accompanied by a vigorous carbonization of the cata-

lyst. At the same time, an optimum nickel to cobalt ratio in the catalysts provides the formation of a carbonization-resistant sample.

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