

Catalytic Materials Based on Hydrotalcite-Like Aluminum, Magnesium, Nickel, and Cobalt Hydroxides for Partial Oxidation and Dry Reforming of Methane to Synthesis Gas

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Abstract—Partial oxidation of methane and dry methane reforming to synthesis gas in the presence of catalysts based on hydrotalcite-like hydroxo salts $[\text{AlMg}_2\text{Ni}_x\text{Co}_y(\text{OH})_{6.08}][(\text{NO}_3)_n\text{H}_2\text{O}]$, where $x = 0, 0.02, 0.04$ and $y = 0, 0.02, 0.04$ with a total Ni and/or Co content of no more than 2 wt % have been first studied. It has been shown that the Ni-containing catalysts provide a synthesis gas yield of 90 and 97% in the case of partial oxidation and dry reforming of methane, respectively; in the presence of these catalysts, a trace amount of carbon nanotubes is formed; the catalyst sample containing both nickel and cobalt does not lead to the formation of any carbon nanotubes during dry reforming of methane.

Keywords: synthesis gas, partial oxidation of methane, dry reforming of methane, cobalt, nickel, Al–Mg hydrotalcite

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Methane reforming to synthesis gas (syngas) is a key stage of the conversion of various types of methane-containing feedstock to petrochemicals. In addition, hydrogen, which is a syngas component, is thought of as an environmentally friendly fuel [1–4]. Promising processes for syngas production include partial oxidation of methane (POM) and dry reforming of methane (DRM). These processes have a number of advantages over the currently available methods based on steam reforming of methane. Thus, POM is an exothermic process; it provides the formation of syngas with the composition $\text{H}_2/\text{CO} = 2$, which is used in the Fischer–Tropsch synthesis of methanol and hydrocarbons. The increasing attention to the DRM process ($\text{H}_2/\text{CO} = 1$) is attributed to the possibility of utilizing carbon dioxide, which is the main greenhouse gas, and the possibility of using biogas, which is a renewable raw material [1–4].

Nickel and cobalt supported on oxides of various chemical origins are known as effective POM and DRM catalysts [1–6]. However, nickel-based catalysts, which exhibit a significantly higher activity than that of cobalt catalysts at relatively low temperatures, being used in DRM, form a considerable amount of surface carbon, which leads to the blocking of the active sites of the catalyst and even to the reactor clog-

ging. The degree of coking of the catalyst can be decreased by selecting a support with required characteristics and admixing nickel with another component, such as cobalt, that will contribute to the oxidation of surface carbon [5].

Some studies of POM and DRM show that it is reasonable to use oxide systems based on Al–Mg hydrotalcite as a catalyst support. At 800°C and short contact times, a catalyst with an atomic ratio of $\text{Ni}/\text{Mg}/\text{Al} = 10/61/29$ (corresponding to a Ni content of 15 wt %) provides the complete conversion of oxygen in a helium-diluted methane–oxygen mixture and methane reforming and a CO and H_2 selectivity of more than 90% [6]. A significant coking of the catalyst is associated with the formation of large nickel particles, which mediate the $\text{CH}_4 = \text{C} + 2\text{H}_2$ and $2\text{CO} = \text{C} + \text{CO}_2$ reactions, whereas POM mostly occurs on small nickel particles (about 120 Å; are not shown in the diffraction patterns). In POM tests with short contact times, a higher temperature at the end of the catalyst bed was recorded; this finding is in contrast with the conventional POM mechanism, according to which, the initial stage of POM is the methane combustion to form CO_2 and H_2O , which react with excess methane to form syngas [6].

Results of POM at 600–800°C depend on the Mg/Al ratio in a hydrotalcite-based catalyst containing 20 wt % Ni [7]. The catalysts were preliminarily reduced in a hydrogen stream. After POM, the samples did not contain a hydrotalcite phase; they contained MgO, NiO, NiAl₂O₄, and metallic Ni phases. It was found that the presence of NiAl₂O₄ hinders the reduction of NiO to the metal. The catalyst based on a sample with Mg/Al = 4.85 and the highest degree of crystallinity showed the best results and the highest coking resistance; this finding is attributed to both the small size of the resulting nickel particles and the presence of the NiAl₂O₄ spinel, which hinders methane dissociation. Above 700°C, oxygen underwent complete conversion; at 800°C, the methane conversion and the H₂ and CO selectivity were 96.5, 95, and 94%, respectively [7].

A Ni_{0.5}/Mg_{2.5}Al catalyst, which was synthesized of a hydrotalcite-like material and had a Ni content of 16.3%, was studied in POM; it provided a methane conversion that was not worse than the value obtained over 1% Rh/MgO [8]. At 800°C, nickel particles with a size of 6–7 nm formed in the reduced catalyst provided a methane conversion of 93%. Data on selectivity are not given by the authors of [8]. Before POM, the reduced catalyst contained phases of MgAl₂O₄, a MgO(NiO) solid solution, and metallic Ni.

A decrease in the Ni content to 5 wt % in a catalyst with Mg/Al = 0.25 and 0.5 [9] provided the formation of POM catalysts that showed nearly 100% methane conversion and CO selectivity values at 900°C. The hydrogen selectivity was about 90%. It should be noted that the reactor was fed with a gas mixture heavily diluted with helium; the catalyst was tested without subjecting to prereduction at a gradual increase in temperature. The formation of syngas began only after heating to 800°C. A decrease in methane conversion and hydrogen selectivity to 90 and 80%, respectively, was observed in a 72-h test. The addition of 5 wt % of gold to the catalysts led to the stabilization of high methane conversion and CO selectivity values and a decrease in the degree of coking; however, it did not affect the hydrogen selectivity. After the reduction of freshly prepared catalysts in a hydrogen stream at 900°C, the diffraction pattern of a sample with Mg/Al = 0.25 exhibited phases of metallic Ni, MgAl₂O₄, or NiAl₂O₄, while crystallized MgO was absent. At Mg/Al = 0.5, only low-intensity broad reflections of MgAl₂O₄ or NiAl₂O₄ were observed. The addition of gold to the catalysts led to an abrupt increase in the intensity of these reflections and the appearance of a reflection of MgO. According to the authors of [9], gold was present in the form of an alloy with nickel.

Extensive studies of nickel catalysts in an aluminum–magnesium oxide matrix were conducted to design coking-resistant DRM catalysts. Thus, a nickel catalyst was supported on the MgAl₂O₄ spinel, which is commonly formed during catalysis with Ni–MgAl-hydrotalcite systems [10]. A 16% Ni/MgAl₂O₄ catalyst prereduced with hydrogen at 550°C exhibited a higher activity in DRM than the activity of catalysts containing 1–2% platinum metals supported on aluminum-stabilized magnesium oxide. Data on conversion and selectivity are not given by the authors of [10]; only turnover numbers of the catalysts are available.

Results of DRM in the presence of catalysts on similar supports varied with varying nickel content in a range of 1–15 wt % [11]. After the hydrogen reduction of the catalyst at 750°C, an undiluted mixture of methane and CO₂ was fed into the reactor at the same temperature. With an increase in the nickel content from 1 to 15%, the methane and CO₂ conversion increased from 72 to 84% and from 85 to 94%, respectively. A simultaneous increase in the catalyst stability was observed; this parameter was monitored during 10 h. The degree of coking increased from 1.5 to 39 wt %. In the presence of a 5 wt % Ni/MgAl₂O₄ catalyst, the methane and CO₂ conversion preserved stable values of 83 and 87%, respectively, for 55 h; the CO and H₂ selectivity varied in a range of 97–99%; the degree of coking was 4.6 wt %. Diffraction patterns of the catalyst after DRM exhibited, along with reflections of MgAl₂O₄, reflections of metallic nickel with a particle size of 10–12 nm.

Catalysts for steam/dry reforming of methane based on nickel-containing MgAl-hydrotalcite have been patented [12]. The catalysts were reduced with hydrogen at 850°C and 20 atm, tested in DRM under the following conditions: 800–900°C, 7–20 atm, a fourfold molar excess of CO₂, and varying amount of supplied steam. At 850°C and 7 atm, catalysts with varying ratio of Ni, Al, and Mg showed close values of methane and CO₂ conversion, namely, 92–96% and 54–69%, respectively. The degree of coking was negligible. Data on DRM are not given by the authors of [12].

The use of aluminum–magnesium hydrotalcites as precursors of DRM catalysts was studied [13]. Nickel was introduced into the precursors by coprecipitation or impregnation; the resulting materials were subjected to calcination to obtain catalysts containing 25 wt % of nickel. The reactor was fed with a nitrogen-diluted mixture of methane and CO₂ under conditions of increasing temperature. The catalysts synthesized either by coprecipitation and or by impregnation did not convert methane at temperatures below 750°C; however, at this temperature, an abrupt increase in the

conversion to 80% was observed. At 800°C, the methane conversion achieved 94% and remained stable for 6 h. The catalyst synthesized by coprecipitation was characterized by the formation of a larger amount of coke per unit mass of the catalyst and a smaller amount of coke per unit surface area. According to X-ray diffraction (XRD) analysis, the spent catalyst contained phases of metallic nickel, magnesium and nickel oxides, and aluminum–magnesium spinel.

The authors of [14] compared the catalytic properties exhibited in DRM by Ni–Al–Mg-hydrotalcite catalysts synthesized by a conventional coprecipitation method and catalysts into which nickel ions were introduced in the form of ethylenediaminetetraacetate (EDTA) complexes. In the latter case, nickel ions were incorporated between the layers in the layered structure of the hydrotalcite matrix as an alternative to the isomorphous replacement of magnesium ions in the hydrotalcite structure. The catalysts were reduced in a nitrogen–hydrogen mixture at 600°C; after cooling in a nitrogen stream, they were heated to 800°C in a stream of a methane–nitrogen–carbon dioxide mixture. Nearly 100% conversion and selectivity values were observed in the presence of a $\text{NiMg}_{11}\text{Al}_{3.3}\text{O}_{17}$ sample, into which nickel was introduced by ion exchange between the MgAlNO_3 hydrotalcite and $[\text{NiEDTA}]^{2-}$, and in the presence of a $\text{NiMg}_{11}\text{Al}_3\text{O}_{16.5}$ sample, which was prepared by exposing a calcined MgAl hydrotalcite to an aqueous solution of $[\text{NiEDTA}]^{2-}$. The catalysts contained about 9 wt % of nickel. A catalyst synthesized by coprecipitation of magnesium and aluminum ions and nickel ions from $[\text{NiEDTA}]^{2-}$ was slightly inferior to the above catalysts. The composition of this material after calcination— $\text{NiMg}_7\text{Al}_2\text{O}_{11}$ —corresponded to a nickel content of 13 wt %. An advantage of this catalyst is a higher coking resistance (5 wt % after 6 h). The two more active catalysts contained 13–15 wt % of carbon after 6 h on-stream; the authors of [14] attributed this fact to the size of the nickel particles in the catalysts. The nickel particle size was 16 nm in the catalyst exhibiting a higher coking resistance and 23–24 nm in the other catalysts.

Ni/Mg/Al DRM catalysts based on a hydrotalcite-like precursor synthesized by coprecipitation with a sodium carbonate solution had a mesoporous structure with a pore diameter of 4–19 nm [15]. Depending on the Mg/Al ratio, their specific surface area varied in a range of 145–220 m²/g. The nickel content was 10% of the sum of magnesium and aluminum oxides (9 wt % of the catalyst weight). The catalyst was reduced in a hydrogen stream at 800°C; an undiluted equimolar mixture of methane and CO₂ was fed. An increase in the Mg/Al ratio from 0.25 to 4 led to a

decrease in the size of nickel particles in the catalysts after DRM from 19 to 11 nm. Catalyst coking ceased at a nickel particle size of less than 15 nm. At varying Mg/Al ratio, the methane and CO₂ conversion values remained almost unchanged at a level of 81–86 and 84–87%, respectively.

DRM in the presence of catalysts similar to those described in [15] yet containing >25% Ni was studied in [16]. The catalyst was reduced in a stream of a nitrogen–hydrogen mixture at 700°C. After that, a nitrogen–diluted mixture of methane and CO₂ in a ratio of 1 : 2 was fed, while increasing the temperature from 500 to 700°C. With an increase in temperature to 700°C, the methane conversion achieved 90–93%, while the CO₂ conversion did not exceed 50%. The more active catalyst contained nickel particles with a size of 5 nm. It was found that it is more advantageous to use catalysts with a molar ratio of $5 > \text{Ni}/\text{Mg} > 1$, $\text{Mg}/\text{Al} > 1/3$, and $\text{M}^{\text{II}}/\text{M}^{\text{III}} = 2$.

Lanthanum-promoted NiMgAl catalysts synthesized of hydrotalcite-like precursors were used in DRM [17–20]. Comparison of the properties of catalysts containing 2 wt % Ni and 0–2 wt % La showed that an increase in the lanthanum content led to a decrease in the activity of the catalysts and an increase in their stability [17]. Tests were conducted at 750°C; reactant conversion values were low (less than 50%). An increase in the Mg/Al molar ratio led to a decrease in the activity of the catalysts and an increase in their stability [18]. In the presence of a catalyst with an atomic ratio of Mg/Al = 2.3, which contained 2.8 wt % of nickel and 1.9 wt % of lanthanum, the CO₂ conversion at 750°C preserved a stable value of about 92% for 300 h; the methane conversion was 2–3% less. The formation of carbon nanotubes and nanofibers was observed. The coking rate was 2 mg/(g_{cat} h) [19, 20].

The authors of [21] report on the synthesis of DRM catalysts, which are referred to as “Co–Al–Mg mixed oxides.” According to the described data, the catalysts synthesized by coprecipitation of nitrates of the above elements with sodium carbonate and subsequent calcination contained 34–53% of cobalt. X-ray diffraction measurements revealed the presence of hardly detectable Co₃O₄ and CoAl₂O₄ phases. The presence of both phases was proved by hydrogen temperature-programmed reduction. Contrary to abundant literature data on a low efficiency of cobalt catalysts in DRM [1–3], after reduction with a hydrogen–nitrogen mixture, the catalyst samples provided relatively high methane conversion values—65%—at a relatively low temperature (550°C). The authors of [21] attributed these results to the promoting effect of magnesium and the presence of a significant amount of Co₃O₄, which undergoes reduction to metallic cobalt more readily than CoAl₂O₄ does. The formation of metallic cobalt was proved by XRD. The catalysts formed a large amount of carbon fibers.

DRM in the presence of Ni–Co–Mg–Al mixed oxides based on precursors of a layered hydrotalcite structure was studied in [22]; the samples were synthesized by coprecipitation from nitrate solutions; after calcination, their composition (in moles) is described as $\text{Co}_x\text{Ni}_y\text{Mg}_z\text{Al}_2$, where x and $y = 0, 1, 2, 3$, and 4 ; $z = 2$ and 4 ; and $x + y + z = 6$. These compositions of oxide precursors correspond to a cobalt and/or nickel content of about 29 or 49 wt %. Hydrogen temperature-programmed reduction and XRD revealed that nickel in a finely dispersed state is present in the precursor matrix, whereas cobalt is capable of forming a Co_3O_4 phase. The catalysts were preliminarily reduced in a hydrogen–argon mixture at 800°C for 2 h and then cooled in argon to 400°C ; after that, an argon-diluted equimolar mixture of methane and CO_2 was fed into the reactor. The temperature in the reactor was gradually increased to 800°C . Throughout the entire temperature range, no significant differences were observed in the CO_2 conversion values obtained in the presence of catalysts with different compositions and different concentrations of nickel and cobalt. Below 700°C , the methane conversion was significantly lower in the presence of cobalt-enriched $\text{Co}_2\text{Mg}_4\text{Al}_2$ and $\text{Co}_3\text{NiMg}_2\text{Al}_2$ catalysts. The same catalysts exhibited a higher coking resistance. At 800°C , methane and CO_2 conversion achieved quantitative values of 93–98%. In this case, the hydrogen and CO yield was 65 and 75%, respectively. According to the authors of [22], despite the close yields of the target products, the highest activity in DRM is exhibited by the $\text{Co}_2\text{Ni}_2\text{Mg}_2\text{Al}_2$ sample containing an equiatomic amount of nickel and cobalt (total content of 49 wt %). XRD revealed the presence of carbon, metallic nickel and cobalt, magnesium oxide, nickel–cobalt carbide, and nickel–aluminum carbide phases in the spent catalysts.

Analysis of the above literature data shows that catalysts based on nickel and cobalt dispersed in an aluminum–magnesium hydrotalcite matrix are promising for use in POM and DRM. The cited authors attribute the activity, selectivity, and stability of these catalysts to the formation of nickel nanoparticles and the presence of magnesium oxide and aluminum–magnesium spinel. In some cases, the addition of cobalt leads to a decrease in the degree of coking of the catalysts. However, all the described catalysts contain a significant amount of nickel and/or cobalt and, in general, are not insusceptible to coking. The known DRM catalysts based on aluminum–magnesium hydrotalcites with a nickel content of less than 5 wt % showed methane and CO_2 conversion values of less than 90% and underwent significant coking [11]; some of the catalysts contained a lanthanum additive, which provided a methane and CO_2 conversion of about 90%, yet did not eliminate the formation of carbon nanofibers and nanotubes [19, 20].

The aim of this study is to synthesize POM and DRM catalysts based on hydrotalcite-like nickel (cobalt)–aluminum–magnesium hydroxo salts with a content of nickel, cobalt, or a mixture thereof of 2 wt % and study the resulting catalysts. The use of these POM and DRM catalysts with an equiatomic ratio of nickel and cobalt at their total content of no more than 2 wt % has not yet been described.

EXPERIMENTAL

Nickel (cobalt)–aluminum–magnesium hydroxo salts used as catalyst precursors were synthesized as follows. At 60°C , under stirring, a solution containing potassium hydroxide and potassium carbonate in a molar ratio of 2 : 1 was dropwise added to a solution containing Al, Mg, Co, and/or Ni nitrates in predetermined amounts to adjust the pH value from 1 to 10. The resulting precipitate was washed with water to remove potassium ions (until a negative sodium tetraphenylborate test). According to chemical analysis and XRD, the resulting three samples of hydrotalcite-like hydroxo salts had the following compositions: $[\text{AlMg}_2\text{Ni}_{0.04}(\text{OH})_{6.08}]\text{--}[(\text{NO}_3)_n\text{H}_2\text{O}]$ (no. 1), $[\text{AlMg}_2\text{Co}_{0.04}(\text{OH})_{6.08}]\text{--}[(\text{NO}_3)_n\text{H}_2\text{O}]$ (no. 2), and $[\text{AlMg}_2\text{Ni}_{0.02}\text{Co}_{0.02}(\text{OH})_{6.08}]\text{--}[(\text{NO}_3)_n\text{H}_2\text{O}]$ (no. 3).

The phase and chemical composition of the synthesized hydroxo salts was determined by chemical analysis and XRD (DRON-2.0 diffractometer, CuK_α radiation); conditions for the formation of the hydroxo salts were controlled by pH-metric titration of solutions on a Radelkis OP-208 precision digital pH meter (Hungary). Element determination procedures are described in [23].

The hydroxo salts were subjected to heating from 20 to 400°C at a rate of $100^\circ\text{C}/\text{h}$ and then held at 400°C for 2 h and at 500°C for 2 h.

The phase composition of the catalysts after POM and DRM was determined on a Rigaku MiniFlex 600 diffractometer (Japan) equipped with a detector with a graphite monochromator and a copper anticathode using CuK_α radiation at $\lambda = 1.54187 \text{ \AA}$. The phase composition was determined using the International Center for Diffraction Data (ICDD) database.

Catalyst morphology after POM and DRM was studied using a Carl Zeiss NVision 40 scanning electron microscope (SEM) equipped with secondary (SE or InLens) and backscattered electron detectors (ESB) at an accelerating voltage of 7 and 1 kV, respectively, and a magnification of up to $200\,000\times$.

The catalytic properties of the samples in POM and DRM were studied in a heated flow-type quartz reactor with a thermocouple pocket. The end of the thermocouple was located in the middle of the catalyst bed. For the POM reaction, the free volume of the reactor was filled with quartz chips. The catalyst precursor powders were pelletized and ground to select a fraction with a grain size of 0.5–1 mm. The weight of

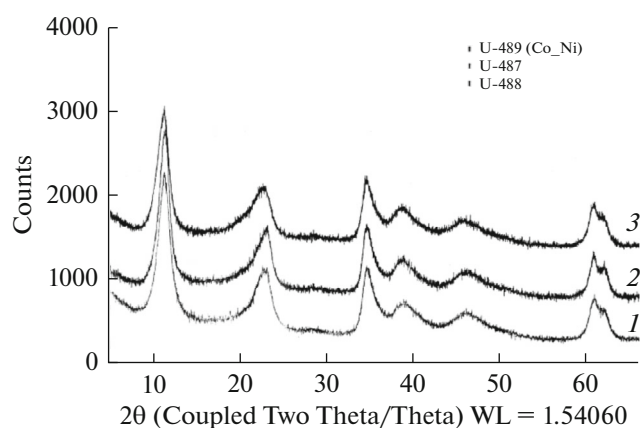


Fig. 1. X-ray diffraction patterns of the synthesized isomorphous samples of hydroxo salts: (1) $[\text{AlMg}_2\text{Ni}_{0.04}(\text{OH})_{6.08}][(\text{NO}_3)_n\text{H}_2\text{O}]$, (2) $[\text{AlMg}_2\text{Co}_{0.04}(\text{OH})_{6.08}][(\text{NO}_3)_n\text{H}_2\text{O}]$, and (3) $[\text{AlMg}_2\text{Ni}_{0.02}\text{Co}_{0.02}(\text{OH})_{6.08}][(\text{NO}_3)_n\text{H}_2\text{O}]$.

the catalyst loaded into the reactor was 0.2 g; the bed height was 1 mm. The reactor was fed with $\text{CH}_4\text{--O}_2$ or $\text{CH}_4\text{--CO}_2$ mixtures undiluted with an inert gas (manufactured at OAO Moscow Gas Refining Plant; purity of 99.9%) at ratios of $\text{CH}_4/\text{O}_2 = 2$ and $\text{CH}_4/\text{CO}_2 = 1$; the flow rate of the gas mixtures was 11–12 and 15–16 L/(g_{cat} h), respectively. The catalyst was heated to a predetermined temperature in a stream of a $\text{CH}_4\text{--O}_2$ or $\text{CH}_4\text{--CO}_2$ mixture for 1 h; after analysis, the temperature was increased or decreased to specified values. Product composition was analyzed by gas–liquid chromatography as described in [5].

Hereinafter, the catalysts synthesized from precursors no. 1, 2, and 3 are referred to as NiHT, CoHT, and NiCoHT, respectively.

RESULTS AND DISCUSSION

The interplanar distances of $d = 1.49(113)$, $1.51(110)$, $1.98(018)$, $2.33(015)$, $2.59(009)$, $3.88(006)$, and $7.76(003)$ Å determined for the initial hydroxo salts are characteristic of a classical hydroxalite-like compound that crystallizes in the hexagonal system and has unit cell parameters of $c = 23.28$ Å and $a = 3.02$ Å (Fig. 1).

Analysis of the cation composition of the samples before calcination gave the following results (wt %): sample no. 1: Al (19.5), Mg (35.2), and Ni (1.95); sample no. 2: Al (20.1), Mg (36.2), and Co (2.0); and sample no. 3: Al (18.6), Mg (34.3), Ni (0.92), and Co (0.92).

According to XRD, after calcination at 400°C (Fig. 2), each of the samples is a mixture of poorly crystallized synthetic corundum and amorphous phases, presumably, of MgO, NiO, CoO, and Co_2O_3 . It is difficult to reliably detect the last three oxides by

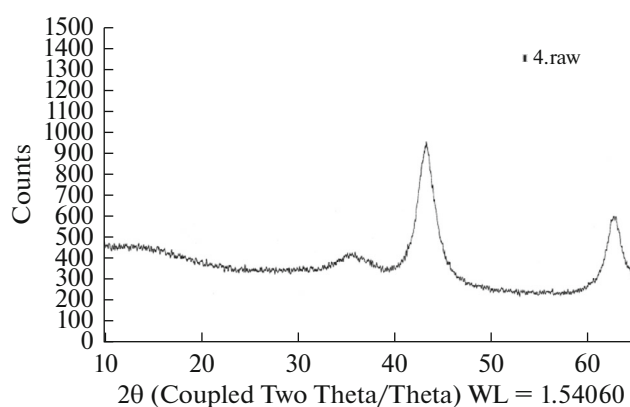


Fig. 2. X-ray powder diffraction pattern of calcined sample no. 3, which contained 18.6% of aluminum, 34.3% of magnesium, 0.92% of nickel, and 0.92% of cobalt before calcination.

XRD because their content in the samples is low. The reflection corresponding to an interplanar distance of $d = 2.08$ Å ($2\theta = 43.5^\circ$) can be identified as the strongest reflection (100% intensity) of synthetic corundum (2016, ICDD database). The reflection at $2\theta = 62.60^\circ$ ($d = 1.48$ Å) and the halo at $2\theta = 35.5^\circ$ ($d = 2.53$ Å) are not identified either for MgO or for any of the described aluminas; they can be attributed to the MgAl_2O_4 spinel or similar structures in which magnesium is substituted by cobalt or nickel [11, 22].

POM test results (Table 1) show that the composition of the catalyst precursor has a significant effect on the results of conversion of a methane–oxygen mixture. The POM products were analyzed after heating the catalyst in a methane–oxygen mixture to 950°C for 1 h and then during decrease in the reactor temperature, as shown in Table 1. It was assumed that these conditions would provide a rapid reduction of nickel and/or cobalt to metals that catalyze POM.

However, it was found that the NiHT catalyst was not fully reduced immediately, as evidenced by the results of tests 1 and 2 in Table 1 at 950°C . Analysis of gases conducted immediately after achieving this temperature showed low reactant conversion and syngas yield values (test 1). However, after a 10-min holding at 950°C (test 2), the catalyst showed methane conversion and syngas yield values of 89–90%, which did not decrease despite the subsequent decrease in the temperature in the catalyst bed (tests 3, 4).

At the same time, it was impossible to transfer the CoHT and NiCoHT catalysts into an active form even by providing a long-term contact with a methane–oxygen mixture at 950°C (Table 1, tests 5, 10). The methane conversion and product yield values were low and significantly decreased with decreasing temperature.

Table 1. POM results for the different catalysts

Test number	<i>t</i> , °C	CH ₄ conversion, %	Yield, %			
			CO	H ₂	CO ₂	C ₂₊
NiHT						
1	950	34	7	14	16	9
2	950	90	90	90	Traces	0
3	920	89	89	89	Traces	0
4	900	89	89	89	Traces	0
CoHT						
5	950	33	5	13	19	8
6	920	32	3	10	20	7
7	900	30	2	8	21	6
8	850	25	2	6	19	4
9	800	25	2	6	21	2
NiCoHT						
10	950	36	7	15	16	8
11	920	32	6	14	18	6
12	900	28	5	12	17	5
13	850	23	3	6	17	4
14	800	23	3	6	17	3

This finding shows that cobalt-containing catalysts based on aluminum–magnesium hydrotalcite with a Co content of 2 wt % or with a Co and Ni content of 1 wt % each are inefficient in POM. At the same time, a similar catalyst containing 2% Ni provided high methane conversion and syngas yield values, which are comparable to the results obtained in the presence of known catalysts with similar compositions with a nickel content of 5–20 wt % [6–9].

The SEM and XRD studies of the catalysts after POM (Fig. 3) showed that their texture and phase composition were approximately the same: a layered structure with occasional inclusions on the surface of particles containing nickel or cobalt, apparently, in the form of oxides. The formation of phases of MgO and spinels containing, along with aluminum, magnesium or nickel and cobalt was recorded.

Thus, the observed differences in the catalytic properties are apparently associated with the presence of cobalt, which hinders the occurrence of POM because of the oxidative activity of cobalt oxides in the presence of oxygen.

As in the set of POM tests, the nickel-free CoHT catalyst provided low methane conversion and syngas yield values in DRM (Table 2). It should be noted that the CO₂ conversion is significantly higher than the methane conversion. After heating to 950°C (Table 2, test 7), the CoHT catalyst was held at this temperature for 30 min to provide a more complete reduction. As a consequence, the reactant conversion and the syngas yield increased, although remained low: the methane and CO₂ conversion did not exceed 28 and 47%, respectively, while the CO and hydrogen yield was 29 and 22%, respectively (Table 2, test 8). In general, a decrease in temperature was accompanied by a decrease in the reactant conversion and syngas yield values (tests 9–12).

In DRM tests in the presence of nickel-containing catalysts, heating in a reactant stream was conducted to 800°C; after that, the temperature was stepwise increased to 950°C and then decreased to 850°C. In the case of the bimetallic NiCoHT catalyst (Table 2, tests 13–18), this procedure led to a gradual increase in the methane and CO₂ conversion to 81 and 85%, respectively, and the CO and hydrogen yield to 83 and 81%, respectively (at 950°C, test 17). The resulting catalyst preserved the achieved high values with a decrease in temperature to 850°C (Table 2, test 18).

The cobalt-free NiHT catalyst provided an abrupt improvement of the DRM results even after heating from 850 to 900°C (Table 2, tests 2, 3). At 950°C, the methane and CO₂ conversion (95 and 99%, respectively) and the CO and hydrogen yields (97 and 95%, respectively) achieved a maximum (test 5); however, these values differed only slightly from the results obtained at 900 and 920°C (Table 2, tests 3, 4). A decrease in the DRM temperature to 850°C (Table 2, test 6) did not lead to a sharp decrease in the reactant conversion and the syngas yield: these parameters decreased to 89%; this value is significantly higher than the results obtained at the same temperature during the heating of the catalyst. In general, all the results show that the presence of cobalt hinders the formation of an active DRM catalyst.

According to SEM and XRD, after DRM, a small amount of carbon nanotubes was formed on the surface of cobalt-free NiHT in the places of localization of nickel-containing particles (Fig. 4). The simultaneous presence of nickel and cobalt in NiCoHT entirely eliminated the formation of carbon nanotubes. Neither cobalt-containing particles nor carbon nanotubes were observed on the surface of DRM-inactive CoHT. The diffraction patterns of the catalysts after DRM did not differ from the diffraction patterns after POM. The results show that the nickel-containing DRM cat-

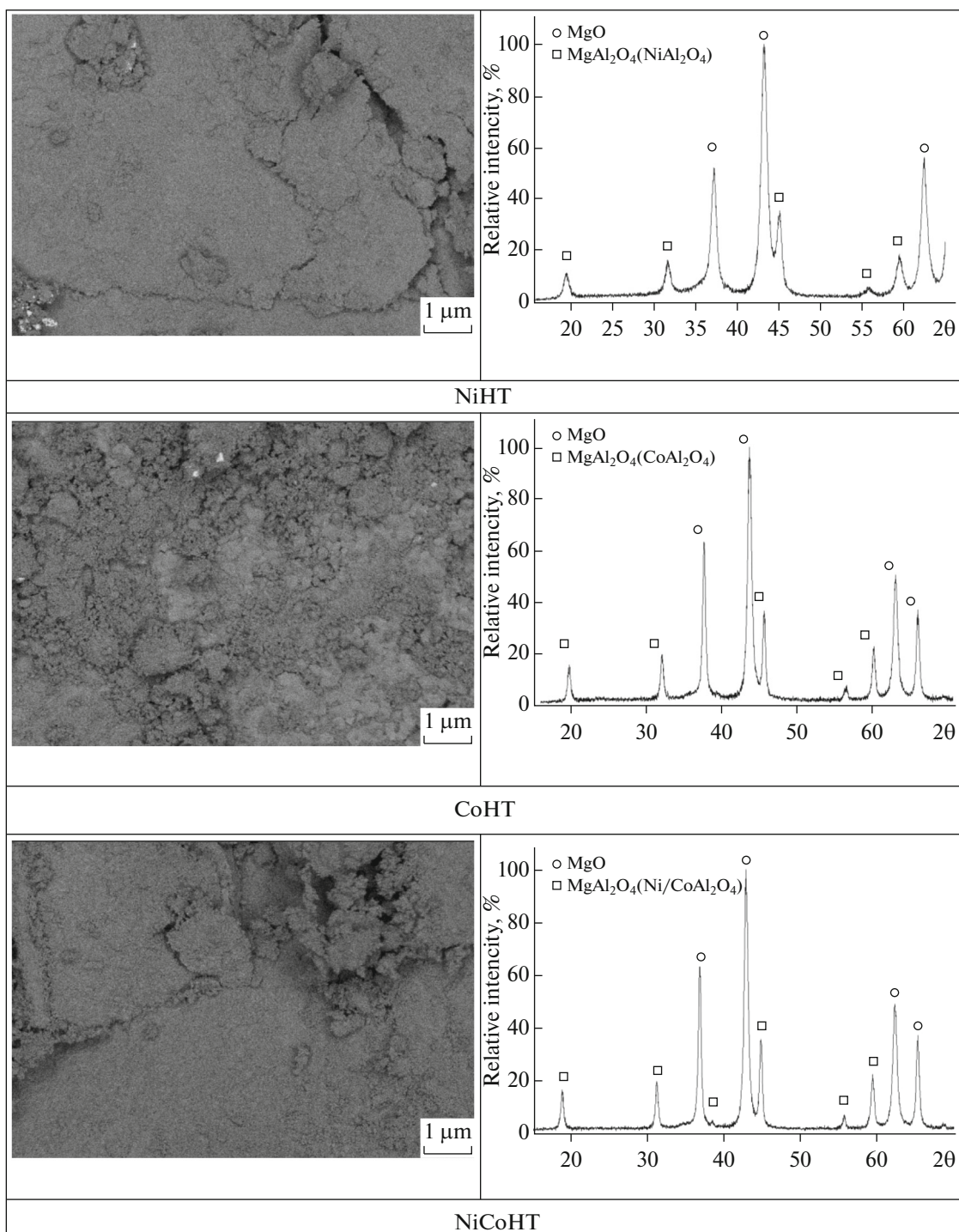


Fig. 3. (left) SEM micrographs and (right) X-ray powder diffraction patterns after POM catalysis.

alysts based on aluminum–magnesium hydrotalcite with a nickel content of 1–2 wt % provide high reactant conversion and syngas yield values; in addition, although the nickel–cobalt catalyst is inferior to the nickel catalyst in the reactant conversion and syngas yield, it entirely eliminates catalyst coking, which is the main disadvantage of the DRM process.

CONCLUSIONS

Catalysts based on hydrotalcite-like hydroxo salts $[\text{AlMg}_2\text{Ni}_x\text{Co}_{0.02-x}(\text{OH})_{6.08}][(\text{NO}_3)_n\text{H}_2\text{O}]$, where $x = 0, 0.01, \text{ or } 0.02$ have been synthesized and studied in the catalytic production of syngas by POM and DRM. The total content of Ni and/or Co in the catalysts (2 wt %) is lower than that in most of the described

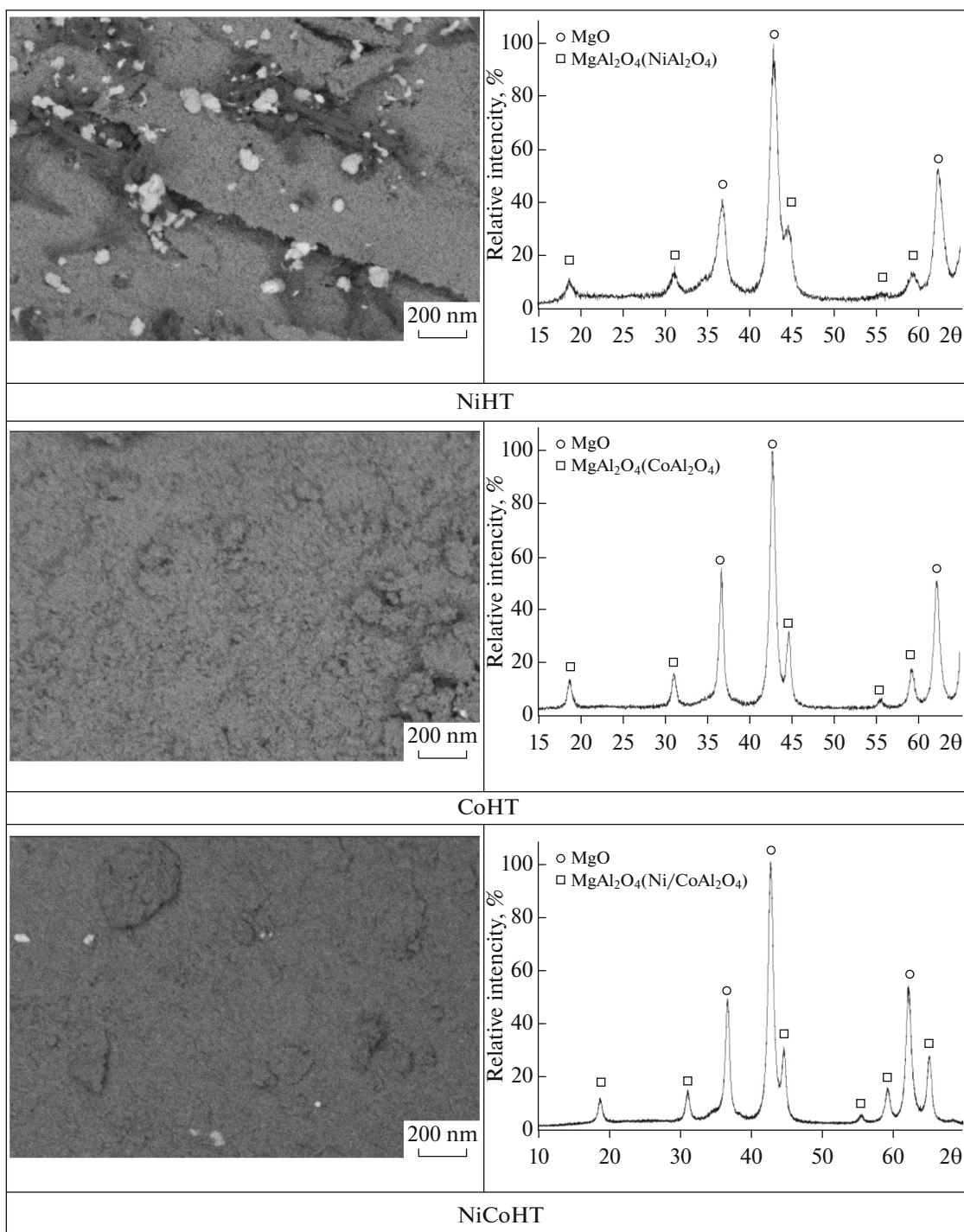


Fig. 4. (left) SEM micrographs and (right) X-ray powder diffraction patterns after DRM catalysis.

counterparts. It has been shown that the Ni-containing catalysts provide a high reactant conversion in POM and DRM and a syngas yield of 90 and 97% in POM and DRM, respectively. A trace amount of carbon nanotubes is formed during DRM in the presence of the nickel catalyst; the catalyst sample containing both nickel and cobalt does not lead to the formation of any carbon nanotubes during DRM.

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Table 2. DRM results for the different catalysts

Test number	<i>t</i> , °C	Conversion, %		Yield, %	
		CH ₄	CO ₂	CO	H ₂
NiHT					
1	800	1	9	1	1
2	850	1	11	5	1
3	900	93	93	92	93
4	920	94	94	94	94
5	950	95	99	97	95
6	850	89	89	89	89
CoHT					
7	950	10	20	10	10
8	950 (after 30 min)	28	47	29	22
9	920	27	42	28	18
10	900	24	40	23	22
11	850	13	26	13	12
12	800	3	16	6	5
NiCoHT					
13	800	6	14	3	Traces
14	850	6	18	3	2
15	900	14	30	12	6
16	920	28	45	28	18
17	950	81	85	83	81
18	850	79	83	81	79

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