Methane Decomposition Nickel Catalysts Based on Structured Supports

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Abstract—New methane degradation nickel catalysts based on original and modified layered double hydroxides and multilayer carbon nanotubes have been synthesized. The synthesized systems have been characterized by a set of physicochemical methods, namely, X-ray diffraction (XRD) analysis, scanning electron microscopy, Raman spectroscopy, and the thermal method. The catalytic activity of the synthesized catalysts in the temperature range of 550–850°C has been studied. It has been shown that in the methane decomposition reaction, the sample with a modified Ni-containing layer exhibits two regions of catalytic activity (550– 650 and 700–850°C), whereas the sample based on carbon nanotubes is characterized by a single region (700–850°C) and the system based on a layered double hydroxide does not show activity in the entire temperature range.

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Climate change taking place in the world is largely dependent on greenhouse gas emissions arising from human activities. The major effect on changes in the average global temperature is exerted by carbon dioxide, whose emission volume is extremely large [1, 2]. Therefore, the development of technologies aimed at decreasing or even completely eliminating carbon oxide emissions is relevant and urgent. A possible direction is the so-called hydrogen power engineering [3]. Hydrogen is thought of as being one of the most environmentally friendly energy sources; it can be used in fuel cells providing the complete absence of CO₂ emissions. However, the main currently available hydrogen production process is the steam reforming of methane; in industry, this process is run under fairly severe conditions (temperature above 800°, a pressure of 20–30 atm) [4]; in addition, carbon oxides are the main waste of the synthesis. Thus, taking into account the full run, which includes the hydrogen production, extraction, and purification stages, hydrogen power engineering is almost equivalent to direct methane combustion in terms of environmental impact. In addition, carbon oxide isolation is fraught with another serious problem, which is associated with the storage and possible further recycling of carbon oxides [5].

A possible method to solve the problem of producing pure hydrogen can be the direct catalytic decomposition of hydrocarbons—mostly methane—via the following reaction: $CH_4 = C + 2H_2$ [6].

In terms of hydrogen power engineering, the process provides the formation of a product without CO and CO₂ impurities, which are poisons for fuel cells; in terms of ecology, the absence of emissions is also an advantage. Carbon can be produced in the form of carbon nanotubes (CNTs) or carbon nanofibers [7–9]. Carbon materials exhibit unique physicochemical (mechanical, electrical, and thermal) properties [10], which contribute to a common use of these materials in modern electronics and engineering, for example, as separators for Li batteries.

The two currently available alternative methane decomposition methods are the homogeneous (noncatalytic) and catalytic methods. The noncatalytic process is based on methane decomposition in the bulk at high temperatures in the absence of catalysts [11-13]. The development of the homogeneous processes is aimed at intensifying the heat transfer; in particular, technologies based on methane decomposition directly in metal melts are being vigorously developed [11, 12].

Catalytic decomposition is commonly implemented with the use of *d*-elements of the iron family (Fe, Co, Ni), of which nickel is reported to be most active in mixed oxide systems [14-17]. The main problem in the practical implementation of the catalytic process is the rapid deactivation of the system, which is associated, first, with the agglomeration of the active metal particles, and, second, with surface carbonization by the resulting carbon structures [18, 19]. A solution to the first problem can be the use of thermostable catalyst systems structured at the nanolevel: for example, systems based on Ni-containing spinels synthesized by the decomposition of the respective layered double hydroxides were proposed [20]. The published data on the catalytic activity of carbon systems suggest that the second problem can be solved by selectively synthesizing catalytically active carbon and metal-containing catalysts based on it [21, 22].

The behavior of modified layered double systems was studied previously [23]; it was found that they are active in hydrogen synthesis. In addition, the formation of CNTs as the main methane decomposition product was observed.

This study is focused on the methane decomposition reaction in the presence of two types of structured catalyst systems, namely, nickel catalysts based on hydrotalcite-like structures and nickel catalyst samples supported on carbon nanomaterials.

EXPERIMENTAL

Sample Synthesis Procedure

The Ni-hydrotalcite sample was synthesized by the pH-controlled coprecipitation method from metal nitrate solutions with a total concentration of Mg, Al, and Ni cations of 1.0 mol/L. A NaOH and Na₂CO₃ solution with concentrations of 2.0 and 0.20 mol/L, respectively, was used as the precipitating agent. Upon the completion of coprecipitation, the precipitate was aged for 24 h. After that, the precipitate was washed and filtered off in a vacuum until a negative nitrate ion test of the washings. The washed precipitate was dried at $100-120^{\circ}$ C to constant weight.

The Ni ethylenediaminetetraacetate (EDTA) sample was synthesized in two stages. At the first stage, Mg,Al-hydrotalcite was synthesized similarly to Ni-hydrotalcite. After that, the resulting hydrotalcite was subjected to thermolysis at a temperature of 550° C. At the second stage, the thermolysis products were placed into a Na₂[Ni–EDTA] solution and held there for 10 h. The resulting Ni–EDTA precipitate was washed and filtered off in a vacuum until colorless washings. The washed precipitate was dried at 100–120°C to constant weight.

Nickel/CNT samples were synthesized by impregnating CNTs with an aqueous solution of nickel nitrate. The CNTs were synthesized by the catalytic pyrolysis of the propane–butane fraction (propane content of 80%) at a temperature of 500°C and atmospheric pressure using nickel catalysts [24]. The resulting CNTs mixed with a catalyst were treated with a hydrochloric acid solution to extract the metals and then functionalized by boiling in concentrated nitric acid. Next, after washing with distilled water and acetone, the CNTs were ground in acetone and then dried and pelletized. The resulting CNTs were subjected to initial wetness impregnation with an aqueous solution of nickel nitrate and then air-dried. After that, they were dried at 100–120°C and calcined at 400°C to decompose nickel nitrate to oxide NiO.

Investigation Procedures

X-ray diffraction (XRD) analysis was conducted on a Rotaflex RU-200 diffractometer (Rigaku, Japan) using CuK_{α} radiation. Nickel oxide NiO crystallite size was determined from peak broadening by the Scherrer formula. Thermogravimetric analysis (TGA) was conducted on a Mettler Toledo TGA/DSC1 instrument. Weighed portions of the test samples (20-26 mg) were placed in 70- μ L alumina crucibles. The samples were heated in an argon medium, while passing argon at a flow rate of 10 mL/min. Temperature programming was used: holding at 30°C for 15 min and heating from 30 to 1000°C at a rate of 10°C/min. Measurement results were processed using the dedicated STARe service routine. The measurement accuracy was $\pm 0.3^{\circ}$ C in determining the temperature and 0.1 µg in determining the weight.

Raman spectra were recorded using a Horiba Jobin Yvon LabRAM HR 800 UV instrument. The spectra were excited using the emission of an argon ion laser at a wavelength of 514.53 nm; the power across the sample did not exceed 7 mW. The signal acquisition time was 200 s.

Micrographs were recorded on a scanning electron microscope coupled with a JSM-6390A X-ray spectrometer (JEOL, Japan).

Catalytic Testing Procedure

Catalytic tests were conducted on a laboratory flow unit with a quartz reactor (Fig. 1).

Two cubic centimeters of silica were charged into the reactor as a substrate; 2 cm³ of a catalyst were loaded at the top; the hot junction of a thermocouple was placed directly in the catalyst bed. Before the test, the catalysts were activated for 2 h as follows: Nihydrotalcite in a H₂ stream at 800°C; Ni–EDTA, in an Ar stream at 420°C; and Ni/CNT, in a H₂ stream at 400°C. After activation, the incipient reaction temperature was set in the reactor (550°C), and methane feeding was started. The tests were conducted under identical conditions for all the catalysts. The relative space velocity was 2000 h⁻¹. Temperature was varied automatically in accordance with the following program: holding for 30 min and heating in increments of



Fig. 1. Diagram of the catalytic unit: (1-3) cylinders with gases, (4-6) pressure regulators, (7-9) valves, (10) Eltochpribor-10M gas flow regulator (GFR), (11) reactor, (12) furnace, (13) hot junction of the thermocouple, and (14) TPM251 oven.



Fig. 2. Methane conversion for the studied samples: (a) Ni-EDTA and (b) Ni/CNT.

50°C for 3 min. Gas sampling for analysis was conducted three times for each mode, namely, 10, 20, and 30 min after beginning.

RESULTS AND DISCUSSION

The sample based on the original hydrotalcite exhibited hardly any activity; the methane conversion in the studied temperature range does not exceed 3%. The dependences of methane conversion on the process temperature under steady state conditions for the Ni–EDTA and Ni/CNT samples are shown in Fig. 2 and Table 1.

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The curve of methane conversion in the presence of Ni–EDTA exhibits a maximum in a range of 600- 650° C, which is a typical range for methane decomposition Ni catalysts [25, 26]. At the same time, it is this region where the most intense decrease in activity occurs during the test; for example, at a temperature of 650° C, the activity decreases more than twofold within 30 min (Fig. 3).

Apparently, in a temperature range below 700°C, nickel localized in the interlayer space of the hydrotalcite undergoes stabilization in a finely dispersed active state. However, carbon deposits partly block the access to methane in the interlayer space. Under certain conditions, Ni-containing systems undergo deactivation

Catalyst	T, °C	Hydrogen content in the produced gas, %	Methane content in the produced gas, %	Hydrogen yield, $g/m^3 CH_4$	Carbon yield, g/m ³ CH ₄	Activity, mol CH ₄ /(g _{Ni} h)
Ni-EDTA	550	8.47	91.53	7.89	23.68	64.59
	600	22.39	77.61	22.51	67.52	184.14
Ni/CNT	650	24.08	75.92	24.45	73.34	200.01
	700	11.77	88.23	11.17	33.50	91.36
	750	21.18	78.82	21.15	63.45	173.05
	800	29.65	70.35	31.08	93.25	254.32
	850	39.53	60.47	43.98	131.95	359.86
	900	40.33	59.67	45.11	135.33	369.09
	550	1.37	98.63	1.23	3.68	13.21
	600	2.32	97.68	2.10	6.29	22.57
	650	3.63	96.37	3.30	9.89	35.50
	700	6.15	93.85	5.66	16.98	60.96
	750	14.34	85.66	13.79	41.36	148.45
	800	24.05	75.95	24.41	73.22	262.79
	850	34.56	65.44	37.31	111.92	401.69

Table 1. Catalytic characteristics of the Ni-EDTA and Ni/CNT samples

owing to carbon encapsulation, which is observed if the carbon deposition rate exceeds the carbon diffusion rate in nickel carbide [22, 23].

The phase composition of the synthesized systems was studied by XRD.

The XRD pattern of the $Mg_{0.78}Al_{0.22}(OH)_2(Ni-EDTA)_{0.11} \cdot zH_2O$ sample (Fig. 4) exhibits characteristic reflections corresponding to reflections of layered double hydroxide ($2\theta = 11.3^{\circ}$, 22.9°, 34.7°, 39.3°,

46.6°, 60.1°); that is, the synthesized compound is isostructural to the $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ hydrotalcite mineral.

According to TGA-differential scanning calorimetry (DSC) data for the Ni-EDTA catalyst (Fig. 5), the sample undergoes stepwise degradation. Up to 220°C, the removal of crystallization water and some of hydroxy groups occurs. The chelating agent undergoes the most vigorous decomposition in a range of



Fig. 3. Variation in the activity of Ni–EDTA during the test. The activity value in Table 1 under respective conditions is taken as the origin (100%).



Fig. 4. X-ray diffraction pattern of the $Mg_{1-x}Al_x(OH)_2(Ni-EDTA)_{x/2} \cdot zH_2O$ sample: filled circles denote reflections of the layered double hydroxide.

380–440°C to form a layered structure intercalated with metallic nickel. With a further increase in temperature up to 1050°C, the layered structure of the hydrotalcite gradually undergoes degradation to form a nickel–aluminum spinel.

The degradation of the layers blocking the active sites is responsible for an increase in catalytic activity with a further increase in catalysis temperature above 700°C. The structure degradation at lower temperatures than the value determined by the TGA–DSC method can be attributed to the partial reduction of the spinel in a methane medium [29]; in addition, carbon deposits also contribute to the degradation of the layers. The total carbon productivity in the test was 0.87 and $2.06 \text{ g}_{\text{C}}/\text{g}_{\text{Ni}}$ in a range of up to 700 and 850°C, respectively.

In the temperature range characteristic of nickel systems, the Ni/CNT catalyst exhibits negligible activity, and the maximum conversion is 3% at 700°C (Fig. 2). In the case of the CNT-containing sample, XRD analysis showed that, prior to the deposition of nickel nitrate (Fig. 6, spectrum *a*), the sample is characterized by reflections $(2\theta = 25^{\circ}, 43^{\circ}, 52^{\circ}, 78^{\circ})$ corresponding to reflections of multi-walled CNTs [30]. After the introduction of a nickel compound into the system (Fig. 6, spectrum *b*), the XRD pattern exhibits reflections corresponding to NiO $(2\theta = 37.3^{\circ}, 62.9^{\circ}, 75.4^{\circ})$. Using data on peak broadening, the nickel oxide crystallite size can be determined by the Debye–Scherrer method. Thus, the coherent scattering region size is approximately 2 nm. Apparently, since nickel

particles are weakly bound to a carbon support, their agglomeration occurs at the reduction stage.

It is known that, at high temperatures, in the absence of active metals, methane degradation can occur directly on carbon supports; in this case, more highly structured carbon systems, such as single-walled CNTs and fullerenes, exhibit the lowest activity [31, 32]. The catalytic properties are determined by surface defects, the presence of which in the Ni/CNT sample is confirmed by Raman spectroscopy and electron microscopy.

Analysis of the Raman spectrum (Fig. 7) suggests that CNTs are multilayer systems, because the spectrum does not exhibit characteristic bands in the lowfrequency spectral region-the so-called radial breathing mode-the presence of which is characteristic of single-walled nanotubes. The intensity ratio between the D band (1375 cm^{-1}), which corresponds to the vibrational mode and is "responsible" for the structural imperfection of the nanotube, and the G band (1616 cm^{-1}), which is responsible for the signal of sp^2 -hybridized carbon, shows the quality of the nanotubes. In the case under study, I(D)/I(G) = 1.429; this value can indicate a high amorphous phase concentration, a high content of imperfect nanotubes, or a significant number of short CNTs, in which edge effects exert the most significant impact.

The evolution of the morphology of CNTs during the catalyst synthesis was studied by electron microscopy (Fig. 8). At each of the synthesis stages, the original CNTs undergo partial degradation.



Fig. 5. Differential thermal analysis curve for the Ni–EDTA sample.

The CNTs washed from the catalyst had the form of pellets of nanotube agglomerates (Fig. 8a). The sizes (outer diameter) of individual original nanotubes varied in a range of 60–90 nm (Fig. 8b). During functionalization, the CNTs undergo shortening and significant compaction (Fig. 8c). After impregnation and calcining, the CNTs preserve their structure only partially; most of them are agglomerates of small fragments with a high amorphous carbon content (Figs. 8d, 8e). The average diameter of the CNTs in this sample is about 80 nm.

The activity of the Ni/CNT and Ni–EDTA samples in the methane decomposition reaction at high temperatures is almost identical. Apparently, after the degradation of the hydrotalcite matrix, catalysis occurs directly on defective carbon deposits similar to the Ni/CNT sample; this factor is also responsible for the extremely low activity of the original hydrotalcite owing to the absence of the stage of formation of imperfect CNTs at low temperatures.

CONCLUSIONS

Two types of catalyst systems—based on layered double hydroxides and CNTs—have been synthesized and studied. It has been shown that, after the introduction of EDTA molecules into the structure of an inorganic composite, the layered structure is preserved; this factor apparently provides the subsequent stabilization of the active Ni-containing component. This fact contributes to the occurrence of two temperature ranges of catalytic activity. The nanotubecontaining sample does not exhibit activity at low temperatures (550–650°C) despite the high degree of dispersion and small size (about 2 nm) of the nickel oxide nanoparticles; this fact can be attributed to particle agglomeration owing to the weak interaction with the carbon support, whereas the catalytic activity corresponds to the reaction that occurs on defects of the CNTs (defect structure is confirmed by Raman spectroscopy) at high temperatures.

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Fig. 6. X-ray diffraction pattern of CNT-containing samples: (a) CNTs and (b) NiO/CNT.



Fig. 7. Raman spectrum of the Ni/CNT sample.

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Fig. 8. Micrographs of the CNTs: (a) a scanning electron microscopy image before functionalization and grinding, (b) a transmission electron microscopy image before functionalization and grinding, (c) a scanning electron microscopy image after functionalization and grinding, and (d, e) calcined samples after impregnation.

CONFLICT OF INTEREST

A.L. Maksimov is editor-in-chief of the *Neftekhmiya* (Petroleum Chemistry) journal. The other authors declare that there is no conflict of interest regarding the publication of this manuscript.

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