



Article Experimental and Simulation Study on Coproduction of Hydrogen and Carbon Nanomaterials by Catalytic Decomposition of Methane-Hydrogen Mixtures

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Abstract: Among all hydrocarbons, the methane molecule contains the highest amount of hydrogen with respect to carbon. Therefore, the catalytic decomposition of methane is considered as an efficient approach to produce hydrogen along with nanostructured carbon product. On the other hand, the presence of hydrogen in the composition of the initial gas mixture is required for the stable operation of the catalyst. In present work, the experiments on the catalytic decomposition of methane-hydrogen mixture were performed in a flow-through quartz reactor equipped with McBain balances under atmospheric pressure. The catalyst NiO-CuO/Al₂O₃ was prepared by the mechanochemical activation technique. The maximum carbon yield of 34.9 g/g_{cat} was obtained after 2 h of experiment at 610 °C. An excess of hydrogen in the reaction mixture provided the long-term activity of the nickel-copper catalyst. The durability tests ongoing for 6 h within a temperature range of 525-600 °C showed no noticeable deactivation of the catalyst. Two kinetic models, *D1a* and *M1a*, were proposed for the studied decomposition of the methane-hydrogen mixture over the nickel-copper catalyst. The kinetic constants for these models were determined by means of mathematical modelling.

Keywords: hydrogen production; methane decomposition; nickel–copper catalyst; nanostructured carbon product; kinetics; mathematical modelling

1. Introduction

In recent decades, global hydrogen production rises up continuously due to its growing demand which comes from various uses such as refining, chemicals, iron and steel, transport, and electricity generation [1]. Hydrogen technologies are considered to be key components to industry and transport decarbonization [2–4]. At the same time, the existing hydrogen production technologies are associated with a number of hardship and disadvantages. Thus, one of the most widely used approaches is steam reforming of natural gas [5–7]. In general, this process is characterized by a relatively low hydrogen yield and a poor quality of the produced hydrogen, which requires an additional treatment and purification from sulfurous gas and CO_2 . The thermal pyrolysis of methane is an alternative approach to producing hydrogen without the CO_2 formation. On the other hand, being realized without a catalyst, this process requires high temperatures (800–900 °C), which makes it energy-intensive. Another issue complicating the worldwide adoption of the methane pyrolysis for the hydrogen production in industry is the undefined application area of the amorphous (non-structured) carbon, which appears as a by-side product.

Contrary, in case of the catalytic pyrolysis of methane, the yield of the target product increases significantly due to the use of various catalysts. The temperature of the process can be noticeably lowered as well. For instance, the use of metallic or carbon-based catalysts allows decreasing the reaction temperature down to 600 °C and even below [8, 9]. Thereby, it is not surprising that many research papers are devoted to the search for the optimal composition of the catalysts and for the appropriate process conditions to decompose methane [10–12]. As is known, such metals as iron, cobalt, and nickel



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). possess activity in catalytic chemical vapor deposition of hydrocarbons with the formation of nanostructured carbon. Therefore, the catalysts based on these metals are applied for the catalytic pyrolysis of methane as well [13,14]. The Ni-containing systems are effective already at temperatures about 550 °C [15], while the Fe-based catalysts begin to work at noticeably higher temperatures [16]. The introduction of a small amount of copper into the composition of Ni-containing catalysts improves their activity, stability and durability [17,18]. The dispersion of the metallic particles is another important issue defining their catalytic performance. Thus, Shen and Lua have reported that hydrogen can be efficiently produced from methane over the dispersed Ni and Ni-Cu particles supported on carbon nanotubes (CNT) [19]. The productivity of such catalysts depends on the exact catalyst's composition and the reaction temperature. It was found that the Ni₇₈Cu₂₂/CNT sample exhibits the stable methane conversion at a level of 80% at 700 °C.

It is important to note that besides hydrogen, the second product of the catalytic pyrolysis of methane over the mentioned metals is nanostructured carbon of given morphology and structure [20,21]. Such carbon is considered as a valuable product, which is attractive for the improvement of physicochemical characteristics of various composite materials, including composites based on cement stone, concrete, different kinds of polymers, lubricants, etc. [22–26]. Therefore, the carbon nanomaterials, including carbon nanofibers (CNF), produced via the catalytic pyrolysis of hydrocarbon sources are highly demanded for their application in material sciences.

As is known, the mathematical modelling is a useful technique which allows shortening of the time required to study different chemical processes. Recently, we have reported the simulation results on hydrogen production via dehydrogenation of alkanes in a catalytic membrane reactor [27,28]. For the process of decomposition of methane-containing mixtures, there is a lack of reported results. Thus, just a few papers devoted to mathematical modelling of the isothermal reactor with both the fixed-bed and moving-bed catalysts were published by Zavarukhin and Kuvshinov [29,30]. Thereby, the study of the process of catalytic pyrolysis of methane-containing mixtures involving the use of mathematical modeling methods is an actual and important task for the development of catalytic technologies for the production of hydrogen and nanostructured carbon.

In order to model any process in the chemical reactor correctly, a reliable kinetic model is required first. In a number of published papers, the process of catalytic methane decomposition is studied, aiming to determine the stage reaction mechanism [31] or to obtain the kinetic model of the process [32,33]. The kinetic models for the decomposition of methane or methane–hydrogen mixtures are reported in the literature for various Ni-based catalysts [33–37]. These models differ in the detailed mechanisms of the reaction as well as in the choice of the limiting stage. For instance, Borghei et al. [33] proposed different kinetic models based on the mechanisms of the dissociative (*D1a*) and molecular (*M1a*) adsorption of methane.

Therefore, this work is devoted to mathematical modeling of the process of catalytic decomposition of methane–hydrogen mixture and is mainly aimed at choosing from existing kinetic models the ones that will most adequately describe experimental data. The efficiency of the nickel–copper catalyst in the process was investigated in a real-time mode using the reactor with McBain balances. Both kinetic models, *D1a* and *M1a*, were applied to simulate the process, and the kinetic constants were determined by comparing the calculated and experimental data for the first time. In the future, after verification of this mathematical model, including the obtained kinetic constants, the optimal conditions of the process will be determined, which will make it possible to scale up this process using the mathematical modeling approach.

2. Materials and Methods

2.1. Synthesis of the Catalyst

The NiO-CuO/Al₂O₃ catalyst was prepared by the mechanochemical activation (MCA) method using a planetary mill "Activator 2S" (LLC Activator, Novosibirsk, Russia). The

schematic diagram of the catalyst preparation approach is shown in Figure 1. Initially, the premix was prepared by mixing the powders of nickel (II) oxide (pure grade, SpectrChem, Moscow, Russia), copper (II) oxide (reagent grade, LLC "Ural Plant of Chemical Reagents", Upper Pyshma, Russia), and aluminum hydroxide (Microintech, Yekaterinburg, Russia). The Ni/Cu atomic ratio was 85/15. The content of the structural promotor (with regard to Al_2O_3) was ~5%. Then, a specimen of the premix (20 g) was loaded into stainless steel jars (250 mL in volume) along with grinding balls (200 g; stainless steel; 5 mm in diameter). Note that the jars were cooled with water to avoid overheating. An industrial frequency inverter VF-S15 (Toshiba Schneider Inverter Corp., Nagoya, Japan) was used to set the rotation frequency of the jars (1856 rpm) and the platform (956 rpm). The estimated acceleration of the grinding balls was 628 m/s² (64 G). After 30 min of activation, the NiO-CuO/Al₂O₃ catalyst was unloaded from the jars in air and separated from the grinding balls using a sieve.



Figure 1. Schematic diagram of the catalyst preparation approach.

2.2. Kinetic Studies on Decomposition of Methane–Hydrogen Mixture

The kinetics of the process of catalytic decomposition of methane-hydrogen mixture over NiO-CuO/Al₂O₃ catalyst was studied under atmospheric pressure using a flowthrough quartz reactor equipped with McBain balances. The principal scheme of the experimental setup is shown in Figure 2. The use of this reactor allows registering the deposition (accumulation) of the carbon product in a real-time mode. A specimen of the catalyst (1.9, 2.9 or 10 mg) was loaded into a basket made of foamed quartz (Figure 2a, position 5). The basket was placed inside the reactor (Figure 2a, position 2) using a quartz thread and a calibrated quartz spring (Figure 2a, position 4). The reactor was fed with an argon flow. The furnace (Figure 2a, position 3) was heated up to 550 °C over 30 min, and the reactor was purged with the argon-hydrogen mixture (5.5 L/h of Ar; 3.6 L/h of H₂) for 5 min to reduce the catalyst. Then, the temperature of the furnace was set to the required value. When the reactor was heated, it was fed with a reaction mixture (pure methane or methane-hydrogen mixture, as further specified). The weight gain of the sample was monitored every 2 min for the first 15 min and every 5 min later on. The duration of the experiments was varied from 1 to 7 h. Finally, the sample with accumulated carbon was cooled down to room temperature in an argon flow, unloaded and weighed. Then, the carbon yield (CY) in grams per gram of catalyst (g/g_{cat}) was calculated as follows:

$$CY = \frac{m(prod) - m(cat)}{m(cat)},$$
(1)

where *m*(*prod*) is a weight of unloaded product, g; *m*(*cat*) is a loading of the initial catalyst sample, g.



Figure 2. Schematic drawing of the setup applied for the kinetic studies (**a**) and exterior view of the reactor (**b**): (1)–vessels with gases; (2)–flow-through quartz reactor; (3)–furnace; (4)–quartz spring; (5)–quartz basket with the sample.

2.3. Characterization of the Samples

X-ray diffraction (XRD) analysis of the catalyst was performed using a Thermo ARL X'tra (Thermo Fisher Scientifics, Basel, Switzerland) diffractometer equipped with a Mythen2R-1D (Dectris AG, Baden, Switzerland) detector. The XRD patterns were registered using a CuK_{α} (λ = 1.5418 Å) radiation in a 2 θ angle range from 10 to 90° at a recording rate of 2°/min.

The morphology of the as-prepared catalyst and the carbon nanomaterials was examined by scanning electron microscope (SEM) on a JSM-6460 microscope (JEOL Ltd., Tokyo, Japan) at magnifications from $8 \times$ to $300,000 \times$.

The high-resolution transmission electron microscopy (HR TEM) images were obtained using a JEM-2010CX microscope (JEOL Ltd., Tokyo, Japan) working at an accelerating voltage of 100 kV with a line resolution of 1.4 Å.

The textural characteristics of the carbon nanomaterials were determined by low-temperature nitrogen adsorption/desorption (Brunauer–Emmett–Teller (BET) method). The adsorption/desorption isotherms were recorded at 77 K using an automated analyzer ASAP-2400 (Micromeritics, Norcross, GA, USA). The preliminary degassing of the samples was carried out at 250 °C for 6 h.

3. Mathematical Modelling of the Process

3.1. Mathematical Model of the Reactor

The mathematical modelling was performed considering the following assumptions:

- 1. The volume of the reaction mixture is constant;
- 2. Any changes in the volume of the reaction mixture caused by the reaction are negligible;
- 3. An ideal mixing mode is realized in the reaction zone.

The inverse task, which is the search of kinetic constants, was solved by the matching method based on the coincidence of the calculated and experimental data obtained during two-hour experiments. Since the catalyst exhibits stability during two-hour experiments, the deactivation of the catalyst was not taken into account in mathematical modeling at this stage of the research.

The non-stationary mathematical model has the following form [38]:

$$V_{\rm mix}\frac{dC_i}{dt} = v_i r \times V_{\rm cat} + G (C_{0i} - C_i); \ i = CH_4, H_2,$$
(2)

$$V_{\rm mix} \frac{dC_C}{dt} = \nu_C r \times V_{\rm cat}.$$
(3)

Initial conditions: t = 0: $C_i = C_{i,in}$; $i = CH_4$, H_2 ; $C_C = 0$.

To solve this equation system, a COMSOL Multiphysics[®] package, version 5.4 (COM-SOL AB, Stockholm, Sweden) was applied.

3.2. Kinetic Model of the Process

The preliminary estimation of the existing kinetic models for decomposition of methane–hydrogen mixtures over nickel–copper catalyst, described by Borghei et al. [33], allows choosing two models for the current research. The *D1a* model based on the dissociative adsorption of methane is described by the following Equation [33]:

$$D1a: r = \left(k^{+} \times P_{\text{CH4}} - k^{-}/K_{r} \times P^{2}_{\text{H2}}\right) / \left(1 + P^{3/2}_{\text{H2}}/K_{r}\right)^{2}.$$
 (4)

The reaction rate equation for the *M1a* kinetic model based on the molecular adsorption of methane is as follows [33]:

$$M1a: r = \left(k^{+} \times P_{\text{CH4}} - k^{-}/K_{r} \times P^{2}_{\text{H2}}\right) / \left(1 + P^{2}_{\text{H2}}/K_{r}\right)^{2},$$
(5)

where k^+ and k^- are obtained using the Arrhenius Euations [39]: $k^+ = k_0^+ \times \exp(-E_a^+/RT)$; $k^- = k_0^- \times \exp(-E_a^-/RT)$.

By solving the inverse task, the activation energy values E_a^+ and E_a^- , as well as the constants k_0^+ and k_0^- providing the best fitting of the experimental points were obtained. In order to calculate the K_r constant, which is $K_r = k_{0r} \times \exp(-E_{ar}/RT)$, the values $E_{ar} = 91.2 \text{ kJ/mol}$ and $k_{0r} = 5.088 \times 10^5 \text{ atm}^{3/2}$ were used.

4. Results and Discussions

4.1. Characterization of the Catalyst

The prepared NiO-CuO/Al₂O₃ catalyst was characterized by XRD, SEM and TEM methods. The obtained results are presented in Figure 3. As follows from XRD data (Figure 3a), the sample is represented by the NiO phase (*Fm3m*, PDF #00-047-1049) only. No copper-containing phases were found that indicate the presence of copper in a roentgen-amorphous state. As for alumina phase, the low level of its content (5%) makes it almost impossible to detect the traces of Al₂O₃ by XRD. For nickel oxide, the lattice parameter was found to be a = 4.1783(3) Å, which is close to the literature data (a = 4.177 Å). The coherent-scattering region is estimated to be ~270 Å. Figure 3b,c shows the SEM and TEM images of the catalyst, correspondingly. As seen, the material is represented by agglomerated particles of irregular shape and few microns in size, which are composed of primary particles of tens of nm in size.



Figure 3. XRD pattern (**a**), SEM (**b**) and TEM (**c**) images of the catalyst prepared by the mechanochemical activation method.

4.2. Kinetic Features of the Decomposition of Methane-Hydrogen Mixture

In general, the catalytic pyrolysis of the methane–hydrogen mixture can be presented by the following reaction scheme:

$$CH_4 + nH_2 \stackrel{cat., T}{\to} C_{(CNF)} + (n+2)H_{2\uparrow}, \tag{6}$$

where $C_{(CNF)}$ is a carbon product deposited in the form of carbon nanofibers.

As long as the catalyst composition is not varied within the present study, just two parameters, the temperature and the hydrogen presence, should be analyzed in detail. Therefore, to study the effects of these parameters on the kinetics of the process, the following conditions have been used: the specimen of the catalyst was 10 mg; the methane flow rate was 24 L/h, and the hydrogen flow rate was 0 or 3.6 L/h. In the durability tests, the specimen of the catalyst was decreased to 2.9 or 1.9 mg, which is reasoned by the higher amount of produced carbon nanomaterial and the volume limitation of the quartz basket.

4.2.1. Effect of the Hydrogen Presence

One of the main reasons leading to deactivation of the catalyst is the blockage of its surface and catalytically active sites by amorphous carbon. Therefore, in order to keep the catalyst in an active state, an addition of hydrogen into the reaction mixture is practiced. Hydrogen interacts with the forming amorphous carbon, thus cleaning the catalyst's surface from these undesirable deposits. The effect of the hydrogen presence in the reaction mixture is demonstrated in Figure 4. In the case of decomposition of pure methane at $600 \,^{\circ}$ C, a rapid deactivation of the NiO-CuO/Al₂O₃ catalyst is observed (Figure 4). The addition of hydrogen into the mixture provides the stable operation of the catalyst during the considered period of the experiment (2 h). It is important to note that the amount of hydrogen released due to the methane decomposition is not enough to stabilize the activity of the catalyst. Thus, when the hydrogen flow was exchanged for an argon flow after 30 min of reaction, the deposition of carbon stopped practically immediately, indicating the deactivation of the catalyst (Figure 4). Thereby, it is evident that an excess of hydrogen in the reaction mixture is required for the stable operation of the NiO-CuO/Al₂O₃ catalyst, and the use of methane-hydrogen mixtures is preferable in terms of efficient catalytic pyrolysis of methane.

It is worth noting that the temperature affects both the kinetics of methane decomposition and the process of the catalyst deactivation. As seen, the rate of carbon accumulation at the decomposition of methane–hydrogen mixture increases with the temperature increase. This effect will be discussed in detail in the next section. The exchange of hydrogen for argon in the composition of the reaction mixture leads to the catalyst deactivation in both cases. However, the deactivation at 600 °C takes place already after less than 5 min (Figure 4, inset). At 550 °C, the catalyst shows even slightly higher activity for the first 10 min without hydrogen if compared with that with hydrogen and only then tends to deactivation. Such an increase in activity can be explained by the reaction equilibrium, since hydrogen is one of the products for the methane decomposition reaction (5).



Figure 4. Effect of the presence of hydrogen in the reaction mixture ($m_{cat} = 10 \text{ mg}$, $G_{CH4} = 24 \text{ L/h}$, $G_{H2} = 0 \text{ or } 3.6 \text{ L/h}$). The inset shows an enlarged area of the main plot.

4.2.2. Effect of the Temperature

A series of experiments on the catalytic pyrolysis of methane–hydrogen mixture at different reaction temperatures was performed in order to find an optimal temperature. The two-hour experimental curves including the values of carbon yield are compared in Figure 5a,b. The noticeable accumulation of the carbon product due to the decomposition of methane–hydrogen mixture is observed starting from 525 °C (Figure 5a). At this temperature, the carbon yield reaches the value of 8.6 g/g_{cat}. A further increase in temperature increases the carbon yield as well. The maximum value of 34.9 g/g_{cat} is observed for the temperature of 610 °C. Then, above this value, an opposite temperature effect is well seen (Figure 5b). Thus, the methane decomposition rate decreases rapidly, and the carbon yield falls down from 30.4 g/g_{cat} at 625 °C to 3.2 g/g_{cat} at 650 °C. Expectedly, the hydrogen yield values show the similar trend within the studied temperature range (Figure 5c).



Figure 5. Carbon accumulation during the methane decomposition in the presence of hydrogen at varied temperatures ($m_{cat} = 10 \text{ mg}$, $G_{CH4} = 24 \text{ L/h}$, $G_{H2} = 3.6 \text{ L/h}$): (**a**) in a range of 500–610 °C; (**b**) in a range of 610–650 °C. The corresponding values of carbon yield (*CY*) are shown below the temperature values. Hydrogen yield for the studied temperatures (**c**).

4.2.3. Studying the Stability of the Catalyst

The stability of the catalyst operation was examined in prolonged experiments. The conditions were as follows. In the 7 h test, the loading of the catalyst was decreased to 1.9 mg, while the gas flow rates remained the same ($G_{CH4} = 24 \text{ L/h}$, $G_{H2} = 3.6 \text{ L/h}$). The temperature was 550 °C. In the 6 h test, the larger amount of the catalyst was used (2.9 mg). In order to keep the contact time ($\tau = V_{cat}/G$) constant, the gas flow rate decreased to the values $G_{CH4} = 6.9 \text{ L/h}$ and $G_{H2} = 1.2 \text{ L/h}$. The process was studied at 525, 550 and 600 °C.

The effect of the catalyst loading is shown in Figure 6a. As seen, a decrease in the catalyst loading of five times does not change the specific carbon yield after 2 h of experiment noticeably. The kinetic curves are practically coincident with each other. This observation can be explained by the fact that a decrease in the catalyst amount at the constant gas flow rates proportionally increases the methane load on the catalyst (G_{CH4}/m_{cat}) as well. Therefore, the same amount of methane is being converted over the catalyst. It should be also noted that no catalyst deactivation is observed during the 7 h experiment for the catalyst specimen of 1.9 mg.



Figure 6. Carbon yield during the decomposition of methane–hydrogen mixture: (**a**) comparison of the catalyst loading; (**b**) comparison of the catalyst loading and the gas flow rates at different temperatures.

Figure 6b compares the kinetic curves for the case when the contact time and the methane load on the catalyst were constant. For all three studied temperatures, a decrease in the catalyst loading affects the kinetics and decreases the carbon yield values. Thus, the carbon yield value diminishes from 33.5 to 25.7 g/g_{cat} at 600 °C, from 15.2 to 9.6 g/g_{cat} at 550 °C, and from 8.6 to 1.3 g/g_{cat} at 525 °C. The 6 h experiments also show no deactivation of the catalyst.

4.3. Characterization of the Carbon Product

As mentioned above, the studying of the methane decomposition process with the formation of carbon product is limited by the volume of the quartz basket used as a sample holder. The photograph of this basket is shown in Figure 7a. During the experiment, the basket is being filled up with the carbon product, which occupies all the available volume (Figure 7b). An analysis of the morphology and the secondary structure of the carbon product was performed using the electron microscopic methods. Figure 8 presents a set of SEM images for the carbon samples obtained via the decomposition of methane–hydrogen mixture at 550, 600 and 625 °C. As seen, regardless of the temperature, the product is represented by carbon filaments of various lengths. These filaments possess the bimodal structure composed of thin (20–100 nm in diameter) and thick (150–350 nm in diameter) fibers. Such a structure indicates that initially the two types of catalyst particles exist. The appearance of the coarse particles can be connected with the reduction stage, which results in such processes as migration, redistribution and agglomeration of nickel and copper oxides.







Figure 8. SEM images of the carbon nanofibers obtained via the decomposition of the methanehydrogen mixture at (**a**,**b**) 550 °C; (**c**,**d**) 600 °C; (**e**,**f**) 625 °C.

The primary structure of the carbon filaments was revealed by the TEM method. As shown in Figure 9, the carbon nanofibers are well-packed ones and belong to a stacked (or

"pile of plates") structural type, which is typical of Ni-catalysts modified with Cu [40]. As seen from Table 1, the produced carbon nanomaterial contains 3–7 wt% of the initial catalyst used for the decomposition of the CH₄/H₂ mixture. The content of the mineral residue (i.e., purity of carbon in CNF product) is determined by the productivity of catalyst (or carbon yield, *CY*). Characterization of the obtained CNF samples by low-temperature nitrogen adsorption allows estimating their specific surface area (*SSA*) and pore volume (*V*_{pore}). The results of BET measurements are also presented in Table 1. It was found that the *SSA* and *V*_{pore} values lie within ranges of 120–174 m²/g and 0.16–0.19 cm³/g, correspondingly.



Figure 9. TEM images of the carbon nanofibers obtained via the decomposition of methane–hydrogen mixture at 625 °C. The magnification is (a) $25,000 \times$; (b) $50,000 \times$; (c) $600,000 \times$.

Table 1. Textural characteristics (specific surface area, *SSA*, and pore volume, V_{pore}) and the content of residual catalyst (*CRC*) for CNF samples obtained via decomposition of CH₄/H₂ mixture over NiO-CuO/Al₂O₃ catalyst at 550, 600 and 625 °C.

#	Temperature, °C	CY, g/g _{cat}	SSA, m ² /g	V _{pore} , cm ³ /g	CRC, wt%
1	550	15.2	174	0.16	6.74
2	600	32.2	147	0.19	3.33
3	625	30.1	120	0.18	3.56

4.4. Estimation of the Kinetic Parameters

As noticed above, a reliable kinetic model is needed for the mathematical modelling of any process. Here, two kinetic models for the decomposition of methane–hydrogen mixture over nickel–copper catalyst were chosen and used [33]. The input parameters applied for the modelling are summarized in Table 2. The simulation results were compared with the experimental points obtained at 525, 550, 600 and 610 °C. This comparison is presented in Figure 10. The mathematical modelling using the *D1a* kinetic model provides an appropriate coincidence of theory with experiment (Figure 10a) at the following values of the parameters: $E_a^+ = 53 \text{ kJ/mol}$; $k_0^+ = 41 \times 10^4 \text{ mol/(m}_{cat}^3 \cdot \text{s} \cdot \text{atm})$; $E_a^- = 17 \text{ kJ/mol}$; $k_0^- = 35 \times 10^2 \text{ mol/(m}_{cat}^3 \cdot \text{s} \cdot \text{atm}^{1/2})$. The *M1a* kinetic model (Figure 10b) fits the experimental points at the following values: $E_a^+ = 63 \text{ kJ/mol}$; $k_0^+ = 14.5 \times 10^5 \text{ mol/(m}_{cat}^3 \cdot \text{s} \cdot \text{atm})$; $E_a^- = 20 \text{ kJ/mol}$; $k_0^- = 35 \times 10^2 \text{ mol/(m}_{cat}^3 \cdot \text{s} \cdot \text{atm}^{1/2})$.

Table 2. The input parameters of the mathematical model.

Parameter	Value	Parameter	Value
Weight of the catalyst (m_{cat}) , mg	10	CH ₄ input concentration $(C_{CH4,in})$, mol/m ³	38.7
Time (t), h	2	H_2 input concentration $(C_{H2,in})$, mol/m ³	5.79
Methane flow rate (G _{CH4}), L/h	24	Volume of the gas mixture (V_{mix}) , m ³	$0.245 imes 10^{-3}$
Hydrogen flow rate (G _{H2}), L/h	3.6	Volume of the catalyst (V_{cat}), m ³	$7.3 imes10^{-9}$



Figure 10. Kinetic modelling of the carbon deposition at various temperatures: (**a**) model *D1a*; (**b**) model *M1a*. Experimental data are shown by symbols, while modelling results are presented by solid lines.

Thereby, at the current stage of study, it can be concluded that both the applied models appropriately describe the experimental data on the catalytic decomposition of methane–hydrogen mixture over the nickel–copper catalyst. The selected kinetic parameters for the models *D1a* and *M1a* provide an acceptable fitting of the experimental points. The further study will be focused on verification of these models and on choosing the most precise model.

5. Conclusions

In present work, the efficiency of the catalytic decomposition of methane–hydrogen mixture over the NiO-CuO/Al₂O₃ catalyst was studied. It was shown that the presence of an excess of hydrogen in the composition of the reaction mixture is necessary to provide the long-term activity and the stable operation of the catalyst. The temperature of the process affects noticeably the kinetics of the process. A temperature range of 600–625 °C is shown to be an optimum in terms of the higher methane decomposition rate and the higher carbon yield. Within this range, the latter exceeds 30 g/g_{cat}. According to the results of electron microscopic characterization, carbon filaments of different length and diameter represent thus obtained carbon product. The product possesses the developed specific surface area (120–170 m²/g) along with relatively low porosity (0.16–0.18 cm³/g). The simulation of this process performed using the two kinetic models, *D1a* and *M1a*, allows defining the kinetic constants, which provide an appropriate fitting of the experimental points. Being verified, the kinetic models along with the defined constants can be applied for the mathematical modelling of the process parameters.

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Nomenclature

- C_i concentration of the i-th component, mol/m³
- *G* flow rate of the gas mixture, L/h
- m_{cat} weight of the catalyst, mg
- *r* rate of the reaction, $mol/m_{cat}^3 \cdot s$
- t time, h
- V_{cat} volume of the catalyst, m³
- $V_{\rm mix}$ volume of the gas mixture inside the reactor, m³
- ν stoichiometric coefficient
- P_i partial pressure of the i-th component, atm
- k^+ rate constant of the direct reaction, mol/(m_{cat}³·s·atm)
- k^- rate constant of the reverse reaction, mol/(m_{cat}³·s·atm^{1/2})

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