

Catalytic Steam Reforming of Methane: New Data on the Contribution of Homogeneous Radical Reactions in the Gas Phase: II. A Ruthenium Catalyst

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Abstract—The kinetics of methane steam reforming and pyrolysis on Ru/Al₂O₃ ($T = 650\text{--}750^\circ\text{C}$, $P_{\text{CH}_4} = 0.001\text{--}0.030 \text{ MPa}$) is studied. The values of the rates and activation energies are compared with the kinetic parameters for nickel catalysts. It was shown that steam reforming can occur on the ruthenium catalyst both heterogeneously and heterogeneously–homogeneously depending on the reaction conditions. Comparative activities of the Ru/Al₂O₃ and Ni–Al₂O₃ catalysts are discussed under the conditions of purely heterogeneous and heterogeneous–homogeneous steam reforming.

INTRODUCTION

Ruthenium catalysts fill a special place among all known catalysts for methane conversion into syngas.

According to [1–3], catalysts based on Ru are more active than nickel catalysts in the steam reforming of methane, as well as in the partial oxidation and carbon dioxide reforming of methane that produce syngas.

When syngas is obtained by the conventional method, steam excess is used to prevent catalyst coking [3]. Partial oxidation and carbon dioxide reforming are carried out under the conditions that are thermodynamically favorable for carbon formation by the reaction $\text{CH}_4 = \text{C} + 2\text{H}_2$. Under these conditions ruthenium systems are among the least susceptible to coking [1–3].

Rostrup-Nielsen [4] assumed that the high resistance of some noble metals, including Ru, to coking can be due to the low mobility and solubility of carbon in the metallic phase that prevent the nucleation of carbon deposits on the metal surface.

According to data from microscopic studies [2], lamellar carbon is observed on the surface of coked ruthenium and carbon filaments are not. Carbon filaments are very typical of nickel, which shows the highest ability to dissolve carbon and the lowest resistance to coking in the partial oxidation and carbon dioxide reforming of methane [1–3].

Available data on the activity of Ru and Ni in the process of methane pyrolysis are contradictory. The article by Rostrup-Nielsen and Bak Hansen [2] is the most frequently cited. They found that the rate of carbon formation in methane pyrolysis on Ni/MgO is much higher than on Ru/MgO. On the other hand, according to Koerts et al. [5], Ru and Ni supported on

SiO₂ show comparable abilities to activate methane in the reaction of its thermal pyrolysis.

Different abilities of Ru and Ni to dissolve carbon and form carbon deposits with different morphologies, their resistance to coking, and comparative activities in methane pyrolysis attract considerable interest in connection with the apparent ranking of their activities (Ru > Ni) in three reactions of syngas formation, which differ in thermodynamic characteristics [1–3].

In the recent book by Arutyunov and Krylov [6], a hypothesis is proposed that the same ranking of the catalyst activities in the steam, oxygen, and carbon dioxide reforming of methane together with other general features of the processes can be evidence for the similarity in the mechanisms of these processes.

Steam reforming of methane has been a research interest for more than 30 years. A widespread opinion is that the process occurs only on the catalyst surface [3].

Recently, we used the flow-circulation method [7] for kinetic studies and obtained new data that show that the steam reforming of methane may occur via both the heterogeneous and heterogeneous–homogeneous mechanisms [8, 9]. Therefore, it is of interest to use the same procedures and techniques to study the possibility of the heterogeneous–homogeneous regime of the steam reforming of methane on ruthenium catalysts.

We expect that the broader range of catalysts used in the mechanistic studies of the steam reforming of methane will allow one to refine the mechanisms of other reactions that produce syngas, and to formulate the requirements to the optimal catalyst for methane reforming.

With this goal, we studied the kinetics of the steam reforming and pyrolysis of methane on the Ru/Al₂O₃

catalyst and compared the kinetic parameters of these two processes for Ru/Al₂O₃ and Ni-Al₂O₃.

EXPERIMENTAL

The study of the steam reforming of methane was carried out in a flow-circulation isothermal reactor made of stainless steel at 650–750°C. Its diameter was 18 mm and the volume was 40 cm³. The concentrations of methane and steam were 33 and 67 vol %, respectively. The capacity V_c of a circulation pump was ~1000 l/h. The initial mixtures were supplied at a rate V equal to 12–57 l/h (3.3–15.9 cm³/s) (Table 1). The compositions of reaction mixtures were analyzed by chromatography.

As can be seen from Table 1, with a decrease in the flow rate of the reaction mixture from 15.9 to 3.3 cm³/s, the conversion of methane at 750°C increased from 40 to 70%. The multiplicity of circulation V_c/V remained several (six to seven) times higher than the minimal value allowable at these conversions X [10] and this multiplicity was sufficient for maintaining approximately constant composition of the reaction mixture. For more details on the procedure of kinetic measurements, as well as on the methods for checking the absence of temperature and concentration gradients on the reactor, see our previous papers [7–9].

The reaction of methane pyrolysis was studied in a quartz reactor with a volume of 15 cm³ with the McBain balance under gradient-free conditions. The temperatures were 650 and 750°C, and the partial pressures of methane were 0.001, 0.010, and 0.030 MPa.

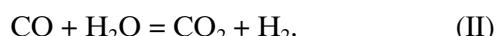
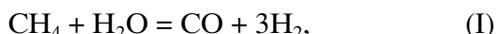
The commercial RK-3 catalyst (supported catalyst containing 0.5% Ru and 99.5% Al₂O₃) was tested. All tests were carried out in the kinetics-controlled regime using the samples with grain sizes ranging from 0.25 to 0.50 mm. In some runs, the samples were diluted with a filler (carbon sorbent) that had a high specific surface area (200 m²/g) [8]. The catalysts were trained before tests using the same program as in [8] for nickel catalysts.

The specific surface area of the catalyst after tests was on the average 40 m²/g. The specific surface area of Ru in the samples was 1.15 m²/g. The specific surface area of the metal was determined using oxygen adsorption.

RESULTS AND DISCUSSION

1. Catalytic Steam Reforming of Methane

Chemical reactions observed in steam reforming can be described by the equations



When the process occurs over an active catalyst (e.g., a nickel catalyst [1–3]), reaction (II) is at equilibrium.

Table 1 and Fig. 1 show the dependence of the apparent rate w of the steam reforming of methane on Ru/Al₂O₃ at 650 and 750°C on the partial pressure of methane in the reaction mixture after the catalyst P_{CH_4} . The amount of the catalyst G was a variable.

The conversion of methane X and the reaction rate w were determined from the primary data from Table 1 as follows:

$$X = \frac{P_{\text{CH}_4}^0 - P_{\text{CH}_4}}{P_{\text{CH}_4}^0}, \quad w = \frac{(P_{\text{CH}_4}^0 - \alpha P_{\text{CH}_4})V}{G100},$$

where $P_{\text{CH}_4}^0$ is the partial pressures of methane in the initial mixture and α is the coefficient that takes into account a change in the reaction volume. The value of this coefficient was determined using the formula

$$\alpha = \frac{0.1 + P_{\text{CH}_4}^0}{0.1 + P_{\text{CH}_4} - P_{\text{CO}} - P_{\text{CO}_2}}.$$

Figure 1 also shows (points A and B) how the dilution of the catalyst with a carbon solvent affects the reaction rate. Table 1 shows the data in the order corresponding to the order of changing the process variables G , T (the reaction temperature), and V (the flow rate of the initial mixture). Each experiment at a given temperature lasted 20–30 min. Analysis of our data led us to the following conclusions:

1. At the same conversions of methane (Table 1), the compositions of the reacting mixtures are the same, and

the ratios $\frac{P_{\text{CO}_2}P_{\text{H}_2}}{P_{\text{CO}}P_{\text{H}_2\text{O}}}$ in all experiments are close to the equilibrium constants of reaction (II) equal to 1.28 and 2.00 at 750 and 650°C, respectively [11]. This points to the fact that in the steam reforming of methane on Ru/Al₂O₃, reaction (II) is close to the equilibrium.

2. The plots of w vs. P_{CH_4} (Fig. 1) are close to those obtained on nickel catalysts [8, 9]. Therefore, for the description of the process rate on Ru/Al₂O₃, we can use the same equation as for nickel catalysts [12]: $w = k(P_{\text{CH}_4} - P_{\text{CH}_4}^*)$. In this equation, P_{CH_4} and $P_{\text{CH}_4}^*$ are the current and equilibrium pressures of methane (at a given temperature and the composition of the reaction mixture) and k is the rate constant of the reaction. This equation is correct at temperatures ranging from 600 to 750°C. At 750°C and higher temperatures, the above equation simplifies: $w = kP_{\text{CH}_4}$.

3. The apparent rate of the reaction depends on the amount of catalyst available in the reactor volume (Table 1 and Fig. 1) in the same manner as in the case of nickel catalysts [8]: with an increase in the amount of the catalyst in the reactor, the apparent rate decreases.

Table 1. Dependence of the apparent rate w of the reaction $\text{CH}_4 + \text{H}_2\text{O}$ on the partial pressure of methane P_{CH_4} at 650 and 750°C and different amounts G of the catalyst Ru/Al₂O₃ in the reaction volume

$V, \text{cm}^3/\text{s}$	Partial pressures in the reacting mixture, $\times 10^2, \text{MPa}$					$X, \%$	$w, \text{cm}^3 \text{CH}_4 (\text{g Cat})^{-1} \text{s}^{-1}$	$\frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}}}$
	P_{CH_4}	P_{CO}	P_{CO_2}	P_{H_2}	$P_{\text{H}_2\text{O}}$			
$G = 3.0 \text{ g}, T = 750^\circ\text{C}$								
8.4	1.46	0.50	0.58	3.90	3.57	43	0.40	1.26
5.4	1.12	0.72	0.59	4.53	3.04	54	0.32	1.22
3.3	0.84	0.90	0.56	5.00	2.71	64	0.23	1.15
15.9	2.01	0.30	0.56	3.15	4.20	28	0.49	1.40
11.7	1.84	0.40	0.55	3.23	3.99	32	0.41	1.13
$G = 3.0 \text{ g}, T = 650^\circ\text{C}$								
8.4	1.88	0.26	0.56	3.12	4.20	32	0.29	1.60
5.4	1.52	0.41	0.62	3.82	3.63	42	0.25	1.59
3.3	1.24	0.50	0.68	4.38	3.22	50	0.18	1.85
15.9	2.41	0.12	0.40	2.00	5.00	18	0.32	1.33
11.7	2.16	0.16	0.50	2.58	4.67	25	0.31	1.73
$G = 1.25 \text{ g}, T = 750^\circ\text{C}$								
8.4	1.14	0.75	0.62	4.56	2.93	53	1.18	1.28
5.4	0.83	0.94	0.56	5.03	2.64	64	0.91	1.14
15.9	1.53	0.44	0.60	3.79	3.65	41	1.72	1.40
11.7	1.32	0.60	0.60	4.18	3.30	47	1.45	1.27
$G = 1.25 \text{ g}, T = 650^\circ\text{C}$								
8.4	1.69	0.36	0.66	3.60	3.70	36	0.80	1.78
5.4	1.43	0.40	0.69	4.06	3.43	44	0.63	2.00
15.9	2.25	0.14	0.45	2.33	4.84	22	0.92	1.55
11.7	1.96	0.30	0.58	3.04	4.12	29	0.90	1.43
$G = 0.52 \text{ g}, T = 750^\circ\text{C}$								
8.4	1.12	0.78	0.62	4.47	2.91	51	2.72	1.22
5.4	0.91	0.90	0.56	4.90	2.74	61	2.09	1.11
3.3	0.62	1.10	0.57	5.40	2.20	72	1.51	1.27
15.9	1.65	0.46	0.56	3.56	3.78	38	3.83	1.15
11.7	1.43	0.55	0.60	4.00	3.43	43	3.20	1.27
$G = 0.52 \text{ g}, T = 650^\circ\text{C}$								
5.4	1.56	0.40	0.66	3.80	3.57	40	1.37	1.76
8.4	1.78	0.32	0.62	3.38	3.90	34	1.81	1.68
11.7	1.98	0.24	0.60	3.00	4.17	28	2.08	1.80
8.4	1.83	0.30	0.60	3.27	4.00	32	1.71	1.60
3.3	1.38	0.50	0.65	4.12	3.35	46	0.96	1.60
$G = 0.25 \text{ g}, T = 750^\circ\text{C}$								
8.4	1.27	0.60	0.60	4.26	3.28	49	5.43	1.30
11.7	1.55	0.45	0.58	3.74	3.72	41	6.33	1.30
15.9	1.72	0.42	0.58	3.46	3.82	35	7.35	1.25
5.4	0.96	0.80	0.62	4.85	2.77	59	4.20	1.36
3.3	0.72	0.95	0.54	5.17	2.62	68	2.96	1.12
$G = 0.25 \text{ g}, T = 650^\circ\text{C}$								
5.4	1.69	0.34	0.65	3.57	3.75	36	2.57	1.80
3.3	1.47	0.40	0.68	3.98	3.47	43	1.87	1.95
15.9	2.37	0.12	0.43	2.10	4.90	19	3.99	1.54
8.4	1.99	0.24	0.62	3.02	4.13	28	3.10	1.90

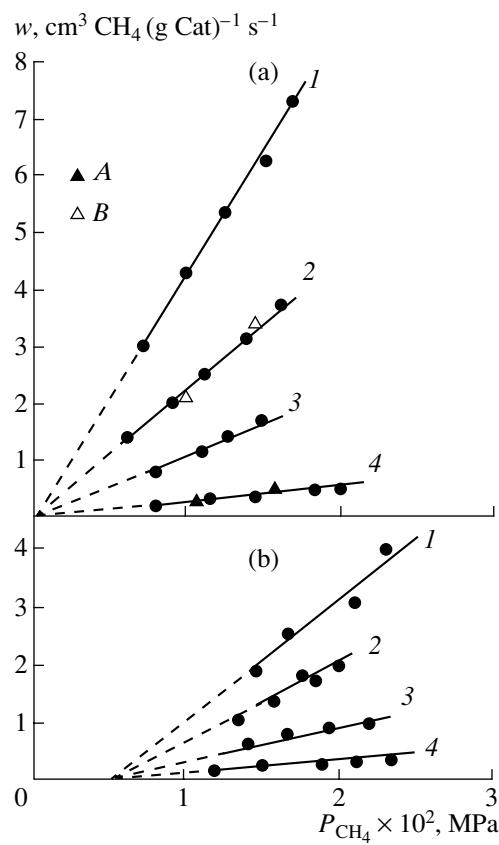


Fig. 1. Dependence of the apparent rate w of the steam reforming of methane on the $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst on the partial pressure of methane P_{CH_4} at (a) 750 and (b) 650°C at different amounts of the catalyst in the reactor: (1) 0.25, (2) 0.52, (3) 1.25, and (4) 3.0 g. Points A refer to catalyst dilution (1 : 5) with the carbon sorbent, and points B refer to the absence of the filler (catalyst loading is 0.52 g).

4. Catalyst dilution with the filler that has a developed surface area (carbon sorbent) does not affect the apparent rate of the reaction if the reactor is charged with a large amount of the catalyst. If a small amount (e.g., 0.5 g) of the catalyst is diluted, the apparent rate (Fig. 1a, straight line 2) decreases to the values that are close to the rates observed for the large amount of the catalyst (Fig. 1a, points A of straight line 4). When the filler is removed by extracting the granules of the catalyst with a magnet, the rate increases to the initial values (Fig. 1a, points B of straight line 2). The same effect was observed in the case of nickel catalysts [8].

We have shown earlier [8, 9] that the above kinetic features of the steam reforming of methane can be explained in the framework of the mechanism that includes both heterogeneous and homogeneous radical reactions.

It is known that, for the heterogeneous-homogeneous processes with nonbranched chain mechanism and chain propagation in the bulk of the gas phase (e.g., the catalytic pyrolysis of methane), the depen-

dence of the reaction rate on the ratio of the catalyst surface to the free volume in the reaction zone (S/V) is typical. An increase in this ratio results in suppressing homogeneous reactions in the gas phase. Analogous dependences of the rate on the amount of the catalyst in the reaction volume observed in the case of the steam reforming of methane are probably due to the catalyst ability to affect the process in a dual manner. On the one hand, the catalyst generates radicals from the surface to the bulk of the gas phase (Arutyunov and Krylov [6] assume that these are methyl radicals) and thus, provides an additional pathway to methane conversion due to the occurrence of radical reactions. On the other hand, as the amount of the catalyst increases, the S/V ratio in the reaction zone also increases. This suppresses homogeneous gas phase reactions and leads to a decrease in the overall reaction rate. The addition of inert filler with a developed surface to the catalyst bed has the same effect.

Kinetic data reported in this work suggest that the steam reforming of methane in the presence of $\text{Ru}/\text{Al}_2\text{O}_3$ can occur in both heterogeneous and heterogeneous-homogeneous regimes.

Figure 2 shows the observed dependences of the apparent rate constant of methane conversion k_{app} on the ruthenium and nickel catalysts (where M is a transition metal) on the amount G of the catalyst in the reactor at 750°C. Figure 2 shows that, when the catalyst loading is 0.2 g, $\text{Ru}/\text{Al}_2\text{O}_3$ is three times more active than $\text{Ni}/\text{Al}_2\text{O}_3$. When the catalyst loading is 3.0–3.5 g, the apparent rate constants are comparable for these catalysts. At 650°C, the dependence of k_{app} on G is analogous. In the case of the small loading (0.2 g), the activities of $\text{Ru}/\text{Al}_2\text{O}_3$ and $\text{Ni}/\text{Al}_2\text{O}_3$ differ by 2.5 times, whereas the activities are close in the case of large loads.

Thus, the above data suggest that the ruthenium catalyst is more active only when the steam reforming of methane occurs in the heterogeneous-homogeneous regime. In the purely heterogeneous regime, the catalyst activities are close.

In connection with this, it is interesting to analyze data reported in [2], where Ru/MgO and Ni/MgO are compared in the steam reforming of methane. Although the authors of [2] consider that this process is purely heterogeneous, the catalyst activities differ by three times. The relation between the activities ($\text{Ru} > \text{Ni}$) is the same as we observed for the heterogeneous-homogeneous regime of steam reforming. At first glance, these findings contradict our data. However, it is important that the activities were tested in [2] in the flow-type microreactor with very small (0.01–0.05 g) loadings of the catalysts diluted with the inert filler MgAl_2O_4 that has a small specific surface area. These conditions are favorable for radical reactions. Therefore, we conjecture that these reactions did take part in the steam reforming of methane under the conditions reported in [2]. This makes it possible to reconcile the results found

in [2] and our data. Note that it is hard to vary the amount of a catalyst in a flow-type microreactor because it is impossible to fulfill and control the conditions of the absence of concentration and temperature gradients in the reaction zone of this reactor.

We have shown in [7] that this limitation is removed when the flow-circulation reactor is used, which provides the absence of both temperature and concentration gradients in the reaction zone and makes it possible to control them. Unfortunately, technical problems in using the flow-circulation method for the studies of the catalytic activity prevents this method from being widely used, especially outside of the Boreskov Institute of Catalysis (Novosibirsk) where a special base for this method was developed.

Among few papers devoted to the use of the flow-circulation methods in the study of the steam reforming of methane, papers of Bodrov *et al.* [13, 14] are known. They studied supported nickel catalysts [13] and nickel foil [14]. On the nickel foil, the reaction was controlled by kinetics, whereas on supported catalysts with grains larger than 1.0 mm, the process was controlled by internal diffusion. This fact prevented Bodrov *et al.* [14] from correct comparisons of the activities of supported and bulk-metal nickel catalysts and the activities of different catalyst loadings.

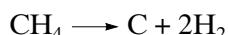
We first reported data on the activities of supported and bulk nickel catalysts for the kinetics-controlled steam reforming of methane in [15]. These experiments confirmed that the reaction occurs via the heterogeneous–homogeneous mechanism on the bulk nickel catalyst and showed that the maximal rates of steam reforming are comparable to the rates obtained on nickel wire [15] and nickel foil [14] only when loadings are small.

The data obtained in this work together with earlier findings [8, 9] show that the highest activity of $\text{Ru}/\text{Al}_2\text{O}_3$ is also achieved when the steam reforming of methane occurs via the heterogeneous–homogeneous mechanism. This activity is much higher than the maximal activity of the nickel catalyst. To refine the maximal rate constant of steam reforming on $\text{Ru}/\text{Al}_2\text{O}_3$, additional data for the activity of the bulk ruthenium are needed.

When the process is purely heterogeneous, $\text{Ru}/\text{Al}_2\text{O}_3$ and $\text{Ni}-\text{Al}_2\text{O}_3$ show the same activity, which is much lower than the activity of these catalysts in the case of the heterogeneous–homogeneous regime.

2. Catalytic Pyrolysis of Methane

For the reaction of methane pyrolysis



on $\text{Ru}/\text{Al}_2\text{O}_3$, the following features are important for comparing these results with data on the steam reforming of methane.

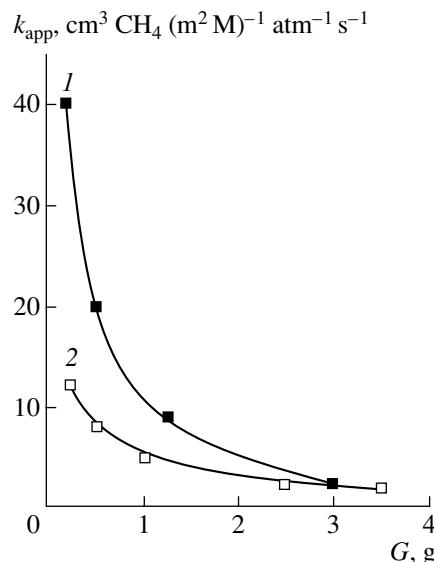


Fig. 2. Dependence of the apparent rate constant of the steam reforming of methane on (1) $\text{Ru}/\text{Al}_2\text{O}_3$ and (2) $\text{Ni}-\text{Al}_2\text{O}_3$ at 750°C on the amount of the catalyst G in the reactor.

One is associated with the mechanism of methane pyrolysis. Because the rate of pyrolysis is characterized by the rate of carbon formation, it is important to make sure that the source of carbon is methane but not ethane or ethylene. They are formed when the process occurs in the heterogeneous–homogeneous regime and decompose at a higher rate than methane [16]. Therefore, we analyzed the compositions of gaseous mixtures after the catalyst bed and showed that C_2 products were not formed in methane pyrolysis under the chosen conditions.

Another specific feature concerns the determination of the rate of methane pyrolysis. In [19], we showed that the maximal activity of the sites for methane pyrolysis over the nickel catalyst remains constant during the first minutes of the reaction when some noncarbonized nickel particles are still present on the surface as seen in the electron microscopic patterns of the samples. We hypothesized that the rate measured during the first 1–2 min of the run characterizes the surface that is close to the surface of the metallic nickel phase. Because the conditions for the study of pyrolysis on ruthenium and nickel catalysts are the same, it is appropriate to use the developed method for the determination of the rate of methane pyrolysis on $\text{Ru}/\text{Al}_2\text{O}_3$, that is, to characterize it by the initial values.

Figure 3 shows the kinetic curves for ruthenium catalyst coking at $P_{\text{CH}_4} = 0.01$ MPa for several temperatures. Changes in the rates of carbon formation with time suggest that ruthenium loses its activity rather rapidly under the reaction conditions. This is because the surface is covered with the so-called capsulating carbon [2]. With an increase in the carbon coverage, the rate of

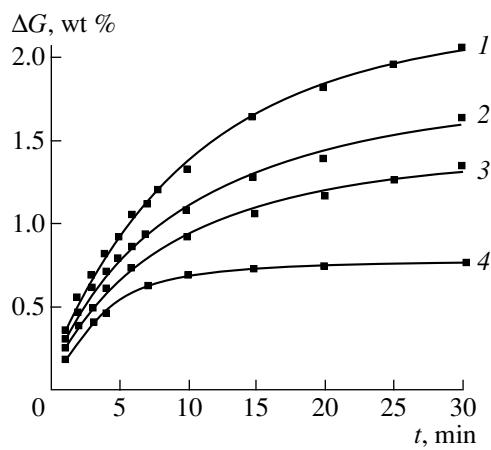


Fig. 3. Changes in the weight ΔG of the Ru/Al₂O₃ catalyst due to the accumulation of carbon in the pyrolysis of methane at $P_{\text{CH}_4} = 0.01$ MPa and T equal to (1) 750, (2) 725, (3) 700, and (4) 650°C.

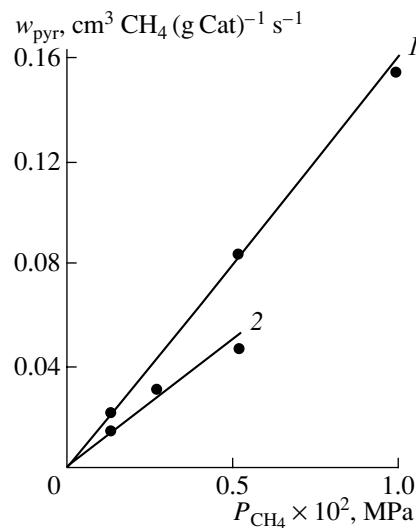


Fig. 4. Dependence of the initial rate of methane pyrolysis w_{pyr} on Ru/Al₂O₃ on the methane pressure at (1) 750 and (2) 650°C. The catalyst fraction is 0.25–0.50 mm. The amount of the catalyst is 0.2 g.

methane pyrolysis on Ru drastically decreases [5]. This is further evidence that the rate of methane pyrolysis on Ru/Al₂O₃ should be measured at the initial period of the reaction. Analysis of the $\Delta G-t$ curves (Fig. 3) shows that, during this period (1–2 min), the process rate is maximal. The morphology of carbon on Ru has an island nature. Therefore, even at $G = 0.25$ wt %, most of the ruthenium surface remains accessible to the reaction.

Figure 4 shows the dependences of the initial rate of methane pyrolysis w_{pyr} on the pressure of methane P_{CH_4} . It can be seen from this figure that the initial rate

of methane pyrolysis on Ru/Al₂O₃ is of the first order with respect to methane as in the case of nickel catalysts [9].

Data shown in Figs. 3 and 4 allow us to calculate the activation energy of methane pyrolysis on the ruthenium catalyst. It is 37 kJ/mol, which is similar to the reference values E_a : 36 kJ/mol [17] and 26 kJ/mol [5].

It is interesting to compare the results obtained for the steam reforming and pyrolysis of methane on ruthenium and nickel [9] catalysts.

Table 2 compares the rates of steam reforming and pyrolysis for two temperatures (650 and 750°C). Table 3 compares the activation energies of these two processes.

It can be seen from these tables that the initial rates and the activation energies of methane pyrolysis on Ru/Al₂O₃ and Ni-Al₂O₃ are close. This points to the fact that ruthenium and nickel show the same activity toward methane activation in this process. The same conclusion follows from [5], where the rate of methane pyrolysis was determined from the amount of hydrogen formed when dilute methane was supplied to the reaction (0.5 vol % CH₄ in He) on the Ru/SiO₂ and Ni/SiO₂ catalysts. On the contrary, according to [2], nickel is more active than ruthenium in methane pyrolysis. This contradicts our findings and findings reported in [5]. In our opinion, this is due to the fact that methane pyrolysis was carried out in [2] at the high concentrations of methane in the initial mixture (95 vol % CH₄). This considerably decreased the accuracy in determining the rates of pyrolysis due to the faster occurrence of the reaction in the initial period.

Tables 2 and 3 also show that the rates and activation energies of pyrolysis and steam reforming are close for both catalysts if the steam reforming of methane occurs over a large amount of the catalyst in the reactor when the conditions are unfavorable for gas-phase reactions and the process occurs on the catalyst surface. We conjecture that in this case, the rates of pyrolysis and reforming are determined by the same rate-limiting step. We have shown earlier [9] that the methane chemisorption step on the catalyst surface with the formation of adsorbed CH₃ radicals and H atoms is such a rate-limiting step. Close values of kinetic parameters for both processes on Ru/Al₂O₃ and Ni/Al₂O₃ point to the fact that, under the conditions favorable for the heterogeneous mechanism, Ru and Ni show the same activity toward methane activation in the rate-limiting step.

For both catalysts (Table 2), the rates of steam reforming on small loadings (w_{reform}^*) are higher than the rates on large loadings (w_{reform}^{**}) and higher than the rate of methane pyrolysis (w_{pyr}). The values of E_a for the steam reforming on small loadings in the reaction volume are also noticeably higher (Table 3). Data from Tables 2 and 3 confirm once again that, when one switches from large to small loadings, the regime of

Table 2. The rates of steam reforming w_{reform} and pyrolysis w_{pyr} of methane on the Ru/Al₂O₃ and Ni-Al₂O₃ catalysts at $P_{\text{CH}_4} = 0.01 \text{ MPa}$

$T, \text{ }^{\circ}\text{C}$	Catalyst	w_{reform}^*	w_{reform}^{**}	w_{pyr}
		$\text{cm}^3 \text{CH}_4 (\text{m}^2 \text{M})^{-1} \text{s}^{-1}$		
650	Ru/Al ₂ O ₃	0.90	0.10	0.09
	Ni-Al ₂ O ₃	0.33	0.12	0.10
750	Ru/Al ₂ O ₃	4.00	0.16	0.14
	Ni-Al ₂ O ₃	1.10	0.19	0.14

* Catalyst loading is 0.2 g.

** Catalyst loading is 3.0–3.5 g.

Table 3. The activation energies of the steam reforming and pyrolysis of methane on Ru/Al₂O₃ and Ni-Al₂O₃

Catalyst	$E_a, \text{ kJ/mol}$	
	steam reforming	pyrolysis
Ru/Al ₂ O ₃	120*	39**
Ni-Al ₂ O ₃	100*	36**

* Catalyst loading is 0.2 g.

** Catalyst loading is 3.0–3.5 g.

steam reforming changes from heterogeneous to heterogeneous–homogeneous. As noted above, in this case, the ruthenium catalyst becomes more active than the nickel catalyst. It is reasonable to assume that in the case of the heterogeneous–homogeneous mechanism of the steam reforming of methane, ruthenium provides a higher concentration of CH_3^{\cdot} radicals in the reaction volume leading to the propagation of homogeneous radical reactions and an increase in the overall rate of the process.

This can be explained by the fact that the CH_3^{\cdot} species bind to the ruthenium surface more weakly than to the nickel surface and the rate of its desorption is higher. Indirect evidence for the weaker Ru–C binding than that of Ni–C is the absence of experimental data on the formation of the bulk carbides of ruthenium, whereas the solubility of carbon in metallic nickel with the formation of metastable carbide is an experimental fact (see, e.g., [18–20]). Therefore, in the case of Ni, the rate of methyl radical desorption is presumably lower and its steady-state concentration on the metal surface is also presumably lower because the participation of adsorbed CH_3^{\cdot} species in the heterogeneous reaction is more active.

The assumption that CH_3^{\cdot} binding to Ru is weaker than to Ni conflicts with the idea of Rostrup-Nielsen [4] and Koerts *et al.* [5], who explain the higher resistance

of ruthenium catalysts to coking by the formation of strongly bound and less mobile carbon species. However, our experimental data are hard to explain in the framework of this idea.

The results of this work allow us to assume that, from the standpoint of the heterogeneous–homogeneous mechanism of steam reforming of methane, nickel and ruthenium show equal abilities to methane activation at the initial stage of the process, which is methane chemisorption with the formation of adsorbed methyl radicals and hydrogen atoms, but they affect the desorption of species to the gas phase in different manners.

CONCLUSION

Our kinetic studies support the heterogeneous–homogeneous mechanism of steam reforming of methane for the ruthenium catalyst. This mechanism was supported earlier for nickel catalysts.

We showed that the steam reforming of methane on Ru/Al₂O₃ is determined by the process conditions, specifically by the organization of the reaction zone. A high ratio of the surface area to the free volume in the reaction zone (the large amount of the catalyst in the reactor) leads to suppressing gas-phase reactions and the validity of purely heterogeneous mechanism. A decrease in the surface area and the S/V ratio in the reaction zone (the small amount of the catalyst in the reactor) is accompanied by the escape of the reaction into the bulk of the gas phase and the realization of the heterogeneous–homogeneous mechanism.

Further refinement of the mechanism of the steam reforming of methane would shed more light on the apparent differences in the activities of Ru/Al₂O₃ and Ni-Al₂O₃.

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