# New Data on Gas-Phase Radical Reactions in the Steam Reforming of Methane in the Presence of Catalysts: I. Nickel Catalysts

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Abstract—Methane pyrolysis and steam reforming were studied over a series of nickel catalysts (Ni–Al<sub>2</sub>O<sub>3</sub>, Ni/MgO, and Ni/LiAlO<sub>2</sub>) under the same conditions (650–750°C,  $P_{CH_4} = 0.001-0.03$  MPa). Unlike heteroge-

neous reaction of pyrolysis, some of the steps of steam reforming of methane occur in the gas phase. When gasphase reactions were suppressed, the rate and activation energy of steam reforming are close to the corresponding kinetic characteristics for pyrolysis. Hypothetically, the rate-limiting step of the process is the dissociative adsorption of methane on nickel in this case.

# **INTRODUCTION**

The steam reforming of methane is a commercial catalytic process for which sophisticated technological problems have been solved, whereas many crucial problems relevant to the theory of this process remain unclear. This primarily concerns its mechanism and the possible existence of steps both in the gas phase and on the surface.

Various mechanisms for the steam reforming of methane have been proposed. All of them assume purely heterogeneous conversion of methane with steam, and the difference is only in the nature of surface species formed during the reaction [1-11].

Several researchers suggested the formation of chemisorbed carbon [4--6]. There were several attempts to correlate the kinetic parameters of methane steam reforming and pyrolysis [6–8]. However, the results of these correlations were contradictory, and they did not shed light on the nature of a rate-limiting step in steam reforming. Bodrov et al. [9] assumed that methane adsorption is rate-limiting. Xu and Froment [10] proposed a mechanism consisting of 13 steps and analyzed each of them as a candidate rate-limiting step. However, such a detailed treatment failed to provide an explanation for all experimental observations, such as a decrease in the rate after replacing H<sub>2</sub>O for CO<sub>2</sub>. Rostrup-Nielsen [1] concluded that there is no single ratelimiting step in this reaction applicable to a broad range of reaction conditions. Aparicio [11] came to the same conclusion.

It is known that, at  $T > 1000^{\circ}$ C, the steam reforming of methane occurs in the gas phase via a radical mechanism without a catalyst [12]. The use of the catalyst leads to a decrease in the process temperature, but this does not exclude the possibility of some gas-phase reactions. Lavrov and Petrenko [13] have hypothesized the possibility for a mechanism with steps in the gas phase and on the surface (a heterogeneous-homogeneous mechanism), but this has not yet found experimental support. We used modern kinetic methods and recently obtained new data suggestive of a heterogeneous-homogeneous mechanism in the steam reforming of methane over nickel catalysts [14, 15]. The specific features of the process may provide additional mechanistic information.

The goal of this study was to examine the reactions of methane pyrolysis and steam reforming over various nickel-containing catalysts and correlate the kinetic parameters of these processes to determine the role of gas-phase reactions in the steam reforming of methane. We also discuss a rate-limiting step in the process of steam reforming.

## **EXPERIMENTAL**

The steam reforming of methane was studied in a flow-type circulation setup [16] at atmospheric pressure, an  $H_2O$  :  $CH_4$  molar ratio of 2, and 650–750°C. Experiments were carried out using a stainless steel reactor (volume, 40 cm<sup>3</sup>; diameter, 18 mm) with a heat exchanger to heat the reaction mixture supplied onto the catalyst. The capacity of a pump was ~1000 l/h. The initial mixtures were supplied at a rate of 10–40 l/h. The compositions of reacting mixtures were analyzed by chromatography.

The flow-type circulation setup maintained the constant temperature of the reactor volume with high accuracy. This was checked by a kinetic method [17]. The maximum drop in the temperature of the mixture in the catalyst bed was at most 0.7°C. To compensate for this heat loss, it was sufficient to keep a temperature differ-

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Catalyst	Ni, wt %	S <sub>sp</sub> , m <sup>2</sup> /g	S <sub>Ni</sub> , m²/g	Rate $\times 10^2$ , cm <sup>3</sup> CH <sub>4</sub> m <sup>-2</sup> Ni s <sup>-1</sup>						E <sub>a</sub> , kJ/mol	
				650°C			750°C				
				W <sub>d</sub>	W <sub>r</sub> <sup>1</sup>	$W_r^2$	W <sub>d</sub>	W <sub>r</sub> <sup>1</sup>	$W_r^2$	Pyrolysis	Conversion
Ni-Al <sub>2</sub> O <sub>3</sub>	21	35	2.4	10	40	4	14	100	15	26	63
Ni/LiAlO <sub>2</sub>	17	16	2.0	6	60	3	8	220	6	23	88
Ni/LiAlO <sub>2</sub>	30	10	2.0	15	40	12	19	190		19	100
Ni/MgO	16	34	4.1	7	30	8	-	_	-	-	84

Kinetic parameters of methane pyrolysis and steam reforming on nickel catalysts

Note:  $P_{CH_4} = 0.01$  MPa,  $W_d$  is the rate of methane pyrolysis,  $W_r^1$  is the rate of methane steam reforming (catalyst loading, 1.0 g), and

 $W_r^2$  is the rate of methane steam reforming for the catalyst diluted by the carbon-mineral sorbent.

ence between reactor walls of  $0.04^{\circ}$ C when the heat flux density was  $0.08 \text{ W/cm}^2$ . This was easy to do in our experiments since we used a flow-type circulation reactor.

Experimental measurements and catalyst preparation were described in detail in our previous articles [14, 16].

The catalytic pyrolysis of methane was studied in a quartz reactor (volume, 15 cm<sup>3</sup>) with the McBain balance. The gradients of temperature and concentrations over the catalyst bed were absent. The sensitivity of weight measurements was  $1 \times 10^{-4}$  g; the relative error in weight measurements was at most 3 wt %. Experiments were carried out at 0.001, 0.01, and 0.03 MPa and 650° or 750°C.

To dilute methane (99.98%), we used argon (99.99%). Gaseous mixtures were supplied into the reactor at a flow rate of 80 l/h. Before kinetic measurements, catalysts were purged with argon for half an hour at room temperature and then heated to 750°C in the flow of H<sub>2</sub>. Then, the catalysts were allowed to stay at this temperature for 0.5 h.

The table shows some characteristics of the catalysts used in this work: the commercial GIAP-16 catalyst (Ni–Al<sub>2</sub>O<sub>3</sub>) and nickel catalysts supported on LiAlO<sub>2</sub> and MgO [18]. The catalysts were granules 0.25–0.50 mm in size. In this case, the reactions under study were not controlled by diffusion. In some experiments, the catalysts were diluted by a carbon-mineral sorbent [19] (granules with a size of 0.5–1.0 mm and a surface area of 200 m<sup>2</sup>/g after tests).

The specific surface area of a sample  $S_{sp}$  was measured by Ar adsorption. The specific surface area of metal  $S_{Ni}$  was measured by oxygen adsorption.<sup>1</sup>

Electron microscopic patterns were obtained using a JEM-100CX microscope with a point resolution of 0.45 nm.

## **RESULTS AND DISCUSSION**

## Catalytic Decomposition of Methane

Methane pyrolysis is currently believed to occur as a heterogeneous-homogeneous process at temperatures above 700°C. Its rate is determined by the reactions of primary homogeneous and/or heterogeneous dissociation of methane (depending on the process conditions, such as temperature, pressure, and the surface vs. volume ratio (S/V) in the reaction zone [20, 21]). The presence of the surface not only lowers the activation energy relatively to the purely homogeneous dissociation of methane [20-26] but affects the nature and distribution of the products from pyrolysis. At low S/Vratios and short contract times, the main carbon-containing products are ethylene, acetylene, and ethane [21]. Over highly dispersed samples with high S/V ratios, the main product is carbon [27].  $C_2$  products decompose at a higher rate than methane [28] and may serve as an additional source of carbonaceous deposits.

Therefore, correct interpretation of experimental findings is only possible when the real "degree of heterogeneity" of the process under chosen conditions is known.

As noted above, the absence of  $C_2$  products at the exit of the reaction zone is the main reason to suggest that methane pyrolysis is heterogeneous. Chromatographic analyses of the composition of gaseous mixtures at the end of the catalyst bed showed that, under our conditions,  $C_2$  products are not formed in noticeable amounts. This points to the fact that under these conditions (temperatures, methane concentrations, and gas flow rates), methane decomposition is purely heterogeneous. In this case, the rate of pyrolysis may be determined from the intensity of carbon accumulation on the catalyst surface.

Figure 1 shows a typical curve for the Ni/LiAlO<sub>2</sub> catalyst coking. Analogous curves were obtained by Pilipenko and Veselov [22] for the kinetics of methane decomposition over promoted nickel catalysts. The curves have two characteristic portions. The first of them is observed during first 5–10 min of a run when

<sup>&</sup>lt;sup>1</sup> We thank V.Yu. Gavrilov for these measurements.

the rate of carbon deposition noticeably decreases. The second portion shows a much slower decrease in the rate. According to Pilipenko and Veselov [22], these changes in the rate of carbon formation are due to the presence of two sites for methane decomposition, one of which is deactivated by carbon; the other is not.

The electron microscopic study confirmed the existence of two sites on the nickel surface. We found that the sites of the first sort are large nickel particles (>1000 A) on which carbon is deposited as a film that blocks the metal surface (Fig. 2A). The sites of the second sort are nickel particles with sizes between 200 and 1000 Å. They initiate a growth of filamentous carbon (Fig. 2B). The ends of filaments are attached to these sites, and the surface is not blocked by carbon deposits. These results agree well with the published data [1, 2].

It is important that the rate of carbon deposition is maximal during the first 1-2 minutes of a run when all active sites for methane decomposition are accessible to the reaction mixture. The electron microscopic patterns of the Ni/LiAlO<sub>2</sub> catalyst (30% Ni) show that, after three minutes of carbon deposition at  $P_{CH_4}$  = 0.01 MPa, only some portion of the nickel particles remains clean. Therefore, the activity of the clean nickel surface is best characterized by the initial rate, which is determined during the first 1–2 min of a run.

The table shows initial pyrolysis rates ( $W_d$ ) per 1 m<sup>2</sup> of nickel surface. It can be seen that these values are independent of the support nature. This fact confirms that the activity toward methane decomposition is determined by the properties of nickel surface,

Figure 3 shows a plot of  $W_d$  versus  $P_{CH_4}$ , which suggests that the first order of the reaction with respect to methane agrees with the kinetic data on methane decomposition at the initial stages of the process [20].

Rostrup-Nielsen [2] reported the Arrhenius plot of methane decomposition over Ni/MgO, suggesting the activation energy  $E_{\rm a}$  of the process at temperatures and pressures similar to those used in this work. At 650- $750^{\circ}$ C  $E_a$ , the activation energy is 21 kJ/mol [2]. A similar value (19–26 kJ/mol) was obtained in this study (see the table). The value of the rate of methane decomposition over the Ni–Al<sub>2</sub>O<sub>3</sub> catalyst measured by us coincides with the rate reported for Ni/MgO under the same conditions (750°C,  $P_{CH_4} = 0.001$  MPa) [2].

There are other examples when our data agree with the literature. Methane activation over Ni/SiO<sub>2</sub> has a barrier of 25 kJ/mol [23]. Two values of  $E_a$  were reported in [22] for nickel catalysts promoted by Re, Mg, Sr, and Ca: 30 and 45 kJ/mol. The presence of two values of activation energies was explained by the existence of active sites for methane pyrolysis of two types. The values of activation energies were also reported for single crystal Ni(111) and Ni(100) surfaces [24-26].

Fig. 1. Kinetics of a change in the weight  $\Delta G$  due to carbon accumulation in the pyrolysis of methane over the Ni/LiAlO<sub>2</sub> catalyst (30% Ni) at  $P_{CH_4} = 0.01$  MPa and (1) T = 750 and (2)  $650^{\circ}$ C.

The initial step of methane conversion is believed to be its dissociative chemisorption [4, 11, 20]:

$$CH_4 \longrightarrow CH_4(ads) \longrightarrow CH_3(ads) + H(ads).$$

An activation energy of 54 kJ/mol for this reaction was measured by Aparicio [11] in his study of the reaction of  $CD_4$  reaction with  $H_2$  on supported nickel.

Avdeev and Zhidomirov [29] estimated the apparent activation energy of methane adsorption on Ni(100) using quantum-chemical methods. The formation of CH<sub>3</sub> and H on the surface had a barrier of 54 kJ/mol, which is of the same order as our experimental values of activation energies (25–54 kJ/mol).

Thus, our data and the data reported by others are suggestive of methane decomposition on nickel catalyst surfaces. The rate of this heterogeneous process is most likely limited by the dissociative adsorption of methane to form methyl radicals and hydrogen atoms on the surface.

#### Catalytic Steam Reforming of Methane

We have found earlier [18] that the steady-state rate of  $W_r$  of the steam reforming of methane is described by the equation  $W_r = k(P_{CH_4} - P_{CH_4}^*)$  at long contact times at 625–750°C, where k is the rate constant, and  $P_{CH_4}$  and  $P_{CH_4}^*$  are the current and equilibrium values of methane pressure. With an increase in temperature,  $P_{CH_{a}}^{*}$  rapidly decreases. At 750°C, the rate law becomes simpler:  $W_{\rm r} = k P_{\rm CH_{\star}}$ . Figure 4 shows the dependence of  $W_{\rm r}$  on  $P_{CH_4}$  for the Ni–Al<sub>2</sub>O<sub>3</sub> catalyst at 650 and 750°C.

Earlier [14, 15] we pointed to the previously unknown kinetic features of the process, such as the dependence of the apparent rate on the amount of the catalyst per



Fig. 2. Electron microscopic pattern of carbon deposits on the Ni/LiAlO<sub>2</sub> catalyst (30% Ni) after coking (for 30 min) by methane at 750°C ( $\times$ 130 000): (A) carbon film deposits and (B) filamentous carbon.

reactor volume under isothermic conditions. We found that, with an increase in the amount of the catalyst, the apparent rate of the reaction substantially decreases. The same effect is seen when the catalyst is diluted with a small amount of an additive with a high specific surface area and a small volume (carbon-mineral sorbent). This enabled us to suggest that the steam reforming of methane in the presence of a catalyst occurs via a heterogeneous-homogeneous mechanism. The catalyst



**Fig. 3.** A plot of the rate of methane pyrolysis on the Ni–Al<sub>2</sub>O<sub>3</sub> catalyst versus methane pressure at (1) 750 and (2) 650°C. The catalyst fraction is 0.25–0.50 mm; the catalyst loading is 0.2 g.

has a dual function: it initiates homogeneous reactions and inhibits them as the reactor is filled with the catalyst, when the general surface area of the catalyst increases and the free volume decreases. The catalyst for heterogeneous-homogeneous methane oxidative coupling works in a similar manner at 800°C [30]: the reactor filling with a catalyst (e.g., MgO) without a diluent (quartz) results in the complete suppression of gas-phase reactions. High-dispersity carbon black has a similar inhibiting action on the process of methane thermal cracking [27].

Comparison of the rates of methane pyrolysis that occurs on the nickel surface and the steam reforming of methane over various catalyst loadings and on the catalysts diluted with a carbon-mineral sorbent is of interest from the standpoint of elucidating the mechanism of steam reforming.

The table and Fig. 5 show relevant data. As can be seen from the table, the rate of steam reforming  $W_r^1$  for equally small loadings (1.0 g) of the nickel catalyst are higher than the rates of pyrolysis  $W_d$  by a factor of 3–10. However, when the carbon-mineral sorbent is added to the catalyst, the specific rates  $W_r^1$  decrease to the values  $W_r^2$ , which are close to the rates of pyrolysis  $W_d$ . This trend in the changes of the rates of methane steam reforming, when an inert diluent is added to the catalyst with a developed surface area, points to the suppression of the reactions in the gas phase and process transition onto the surface.

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**Fig. 4.** A plot of the rate of  $W_r$  of methane steam reforming of the Ni–Al<sub>2</sub>O<sub>3</sub> catalyst versus methane pressure at (a) 750 and (b) 650°C for the following catalyst loadings: (1) 0.2, (2) 0.5, (3) 1.0, and (4) 3.5 g (the catalysts without a diluent). The catalyst fraction is 0.25–0.50 mm.



**Fig. 5.** A plot of (2, 4) the apparent rate  $k_{app}$  at 750°C, (1, 3) activation energy  $E_a$  of (1, 2) steam reforming and (3, 4) methane reforming on the Ni–Al<sub>2</sub>O<sub>3</sub> versus weight of catalyst loading (G) (the catalyst without a diluent).

Figure 5 compares the results of kinetic parameters of the two reactions on the best studied  $Ni-Al_2O_3$  catalyst. As can be seen from this figure, in the case of small loadings, the apparent rate constant of steam reforming is much higher than the rate constant of its decomposi-

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tion. However, the apparent rate constant of steam reforming decreases with an increase in the weight of loadings and becomes close to the rate constant of methane decomposition. Interestingly, unlike in steam reforming, the rate constant of methane pyrolysis remains virtually the same under our conditions when the weight of the catalyst loading changes by a factor of ten. This may be evidence for the heterogeneous nature of pyrolysis.

The calculation of the activation energy of methane steam reforming showed that  $E_a$  decreases from 105 kJ/mol for 0.2 g of the catalyst to 20 kJ/mol for 4.5 g together with the rate constant. The latter value of the activation energy probably corresponds to the activation energy for methane interaction with nickel to form adsorbed methyl radicals and hydrogen atoms

## CONCLUSION

The results of this work support an earlier assumption that the steam reforming of methane is a heterogeneous-homogeneous process in the presence of a nickel catalyst. A change in the filling of the reactor with the catalyst affects the rate and the value of the apparent activation energy of the process. An increase in the catalyst loading and/or the addition of an inert sorbent that adsorbs active radicals from the gas phase decreases the apparent rate constant and the activation energy because of the suppression of gas-phase radical reactions, which is characteristic of the transition from a heterogeneous-homogeneous to a purely heterogeneous mechanism.

After comparing the kinetic parameters for the processes of methane decomposition and steam reforming, we suppose that in the case of a heterogeneous mechanism of the steam reforming of methane, the rate of the process is determined by methane adsorption on nickel with the formation of adsorbed hydrogen and methyl.

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