Steady-state kinetics and mechanism of methane reforming with steam and carbon dioxide over Ni catalyst

A.K. Avetisov [a,*], J.R. Rostrup-Nielsen [b], V.L. Kuchaev [a,✠], J.-H. Bak Hansen [b], A.G. Zyskin [a], E.N. Shapatina [a]

[a] Karpov Institute of Physical Chemistry, 105064 Vorontsovo Pole 10, Moscow, Russia
[b] Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark

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ABSTRACT

A critical analysis of known kinetic models of methane reforming on Ni-catalyst is performed. Based on new own and known published experimental data a microkinetic model of steam and dry methane reforming on Ni-catalyst is proposed and proved. The model eliminates drawbacks of the known previous models. The kinetic equations are derived. Kinetic parameters of the model are adjusted by means of mathematical modeling with the use of own and published data. Pore-diffusion resistance was taken into account during calculations. The obtained values of kinetic parameters agree with the estimated ones obtained according to the transition state theory.

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1. Introduction

A significant part of Mikhail Temkin's scientific activity was devoted, along with thermodynamics and electrochemistry, to the study of kinetics and mechanisms of heterogeneous catalytic reactions [1] under stationary conditions. Most of these investigations have been performed by Temkin et al. in Karpov Institute of Physical Chemistry, where he was the head of the laboratory of chemical kinetics for about 50 years. Of special importance are kinetic models for stationary complex reactions because catalytic reactors normally operate under steady state conditions.

The study of mechanisms of catalytic reactions was based on comprehensive kinetic investigations. Temkin was one of the first who began to use circulation flow units [2]. This gives the possibility to derive one-parametric dependences of the reaction rates on partial pressures of the reaction mixture components. This makes the experimental justification of the proposed kinetic equations more reliable.

The kinetic models suggested by Temkin could be somewhat simplified ones. Thus, his kinetic models often include collision steps, that is, the interaction of a molecule from the gas phase with an adsorbed particle (linear mechanisms). This simplifies the derivation of explicit kinetic equations and makes easier the fitting parameters entering these equations. The latter was very important taking into account the absence of any computing facilities at the beginning of Temkin's activity or the absence of high-speed computers later.

1.1. Temkin et al. model

One of industrial-scale reactions which have been studied by Temkin and co-workers is steam reforming of methane

$$CH_4 + H_2O = CO + 3H_2 \tag{1}$$

$$CO + H_2O = CO_2 + H_2 \tag{2}$$

$$CH_4 + 2H_2O = CO_2 + 4H_2 \tag{3}$$

Based on new experimental data, in the present work we propose and validate the mechanism of steam and dry reforming of methane over nickel catalysts. This mechanism is an advancement of the mechanism proposed by Temkin in [3]. Kinetic equations are derived and kinetic parameters are obtained.

As was pointed by Temkin and co-workers [4], in methane steam reforming at temperatures 700–900 °C commonly used in practice, it is difficult to avoid diffusion restrictions of the reaction, even for fine catalyst grains of commercial supported catalysts. To be sure that the reaction proceeds in the kinetic region, nickel foil was used as a catalyst.

Steam reforming of methane as well as the reverse reaction of carbon monoxide hydrogenation was studied under gradientless conditions using a glass circulation flow unit [3]. In most detail, the kinetics of methane reforming has been studied at catalyst temperatures 470, 500, 600 and 700 °C and atmospheric pressure.

Experimental data were described based on the following two-route ($N^{(1)}$, $N^{(2)}$) reaction scheme

	$N^{(1)}$	$N^{(2)}$
(1) $CH_4 + Z \rightleftarrows ZCH_2 + H_2$	1	0
(2) $ZCH_2 + H_2O \rightleftarrows ZCHOH + H_2$	1	0
(3) $ZCHOH \rightleftarrows ZCO + H_2$	1	0
(4) $ZCO \rightleftarrows Z + CO$	1	0
(5) $Z + H_2O \equiv ZO + H_2$	0	1
(6) $ZO + CO \equiv Z + CO_2$	0	1

(A)

$N^{(1)}$: $CH_4 + H_2O = CO + 3H_2$.
$N^{(2)}$: $CO + H_2O = CO_2 + H_2$.

Here Z means a free adsorption site on nickel surface, Z preceding chemical formula means the corresponding chemisorbed particle, and symbol $\equiv$ means a quasi equilibrium reaction. On the right side of elementary steps stoichiometric numbers for these steps are given. Such numbers could be negative, positive or equal to zero [1]. Under the assumption that the surface coverage by CH_2, CHOH, and CO species is much lower than unity, the kinetic equation for methane consumption rate via route $N^{(1)}$ has the form

$$r = \frac{k_1 P_{CH_4}(1 - x_{(1)})}{(1 + l_1 P_{H_2O} + l_2(P_{H_2}^2/P_{H_2O}) + l_3(P_{H_2}^3/P_{H_2O}))(1 + K_5(P_{H_2O}/P_{H_2}))} \tag{4}$$

where k_1, k_2, k_3, k_4, k_{-1}, k_{-2}, k_{-3}, k_{-4} are the rate constants of corresponding elementary steps; $l_1 = k_{-1}/k_2$, $l_2 = k_{-1} \cdot k_{-2}/k_1 \cdot k_2$, $l_3 = k_{-1} \cdot k_{-2} \cdot k_{-3}/k_2 k_3 k_4$, and K_5 is the equilibrium constant of step 5.

Eq. (4) was successful in the description of experimental data through data fitting with the use of theoretical expressions for pre-exponential factors of rate and equilibrium constants. The term $l_1 P_{H_2O}$ appeared to be much smaller than unity and might be neglected for conditions of experiments in [3]. Similarly, the term $K_5 P_{H_2O}/P_{H_2}$ is also negligible.

Let us discuss in more detail some features of mechanism (A).

The reaction proceeds via dissociative adsorption of methane on nickel accompanied with the liberation of hydrogen molecules in the gas phase. At sufficiently low partial pressures of hydrogen surface species ZCH_2 react faster with water molecules; thus methane adsorption becomes essentially irreversible and the reaction rate of methane consumption is described by the equation

$$r = k_1 P_{CH_4}(1 - X_{(1)}), \tag{5}$$

where $X_{(1)} = (P_{CO} P_{H_2}^3 / K_1 P_{CH_4} P_{H_2O})$ reflects how close the reaction (1) is to equilibrium, K_1 is the equilibrium constant of reaction (1).

The values of l_2 and l_3 in Eq. (4) decrease with temperature in such a way that within the studied range of partial pressures of the reaction participants the retarding action of hydrogen and the accelerating action of water becomes insignificant at 600 °C and completely disappears at 700 °C. At temperatures lower than 600 °C it is necessary to use Eq. (4), although it should be mentioned that for these temperatures a region of transition to Eq. (5) was observed. The validity of Eq. (5) for the rate of methane reforming was shown also in [5,6].

According to mechanism (A), the reasons of deviations from Eq. (5) are related with the fact that at increasing hydrogen partial pressure, the step 1 becomes fast enough in the reverse direction, the methane adsorption becomes reversible, and a reaction retardation by hydrogen is observed according to Eq. (4). In this case, the increase in the steam partial pressure results in the decrease in surface coverage with ZCH_2 species and in the decrease in the methane desorption rate. Therefore, at high partial pressures of hydrogen the acceleration of reaction with steam is observed.

It should be noted that since the reaction was performed on nickel foil in a gradientless circulation flow system, its kinetics cannot be affected by pore-diffusion resistance or by heat and mass transfer resistance. Note also that the second term in the denominator of Eq. (4) appears due to surface coverage with oxygen atoms, in accordance with the equilibrium step 5. While fitting experimental data of [3] the value of this second multiplier was found to be close to unity, and hence, the surface coverage with oxygen may be neglected.

Thus, according to the mechanism by Temkin and co-workers [3], under conditions of their experiments on steam reforming of methane, the surface coverage with all adsorbed species is much smaller than one.

Mechanism (A) is extremely simplified; however, it correctly conveys the physical meaning of the dependence of reaction rates on partial pressure of the reaction mixture components.

1.2. Froment and Xu model

More resent publications [7–9] containing new experimental data show that the mechanism above needs more detailed elaboration. For instance, it is reasonable to accept that the formation of carbon dioxide may proceed via the interaction between an oxygen atom adsorbed on the nickel surface and an adsorbed CO molecule rather than via collision of CO molecule from the gas phase. Additionally, it is probable that adsorbed H atoms also participate in the reaction steps. Furthermore, a modification of the mechanism is necessary in order to describe kinetic data at elevated pressures. The modified mechanism of methane reforming with water steam and carbon dioxide will be explained later, after the analysis of these publications.

Methane steam reforming was studied [7,8] in plug-flow systems mainly at 550 °C as well as at 500 and 525 °C, and the total reaction mixture pressure from 3 to 15 bars. The ratio of partial pressures of hydrogen to methane at the reactor inlet was 1.25, and that of water to methane was 3 or 5. The contact time was varied by changing the feed rate of the reaction mixture over a wide range. The catalyst had the form of grains of the size 0.18–0.25 or 0.3–0.4 mm.

The experiments have shown that, in a similar manner to the results of Temkin and co-workers [3], the rate of methane consumption decreased with increasing hydrogen partial pressure and increased with increasing steam partial pressure. The order of the methane consumption rate with respect to methane was significantly lower than unity. The experimental data were described on the basis of the following mechanism:

	$N^{(1)}$	$N^{(2)}$	$N^{(3)}$
(1) $H_2O + Z \rightleftharpoons ZO + H_2$	1	1	2
(2) $CH_4 + Z \rightleftharpoons ZCH_4$	1	0	1
(3) $ZCH_4 + Z \rightleftharpoons ZCH_3 + ZH$	1	0	1
(4) $ZCH_3 + Z \rightleftharpoons ZCH_2 + ZH$	1	0	1
(5) $ZCH_2 + ZO \rightleftharpoons ZCH_2O + Z$	1	0	1
(6) $ZCH_2O + Z \rightleftharpoons ZCHO + ZH$	1	0	1
(7) $ZCHO + Z \rightleftharpoons ZCO + ZH$	1	0	0
(8) $ZCO + ZO \rightleftharpoons ZCO_2 + Z$	0	1	0
(9) $ZCHO + ZO \rightleftharpoons ZCO_2 + ZH$	0	0	1
(10) $ZCO \rightleftharpoons CO + Z$	0	1	0
(11) $ZCO_2 \rightleftharpoons CO_2 + Z$	0	1	1
(12) $2ZH \rightleftharpoons ZH_2 + Z$	2	0	2
(13) $ZH_2 \rightleftharpoons H_2 + Z$	2	0	2

(B)

$N^{(1)}$: $CH_4 + H_2O = CO + 3H_2$.
$N^{(2)}$: $CO + H_2O = CO_2 + H_2$.
$N^{(3)}$: $CH_4 + 2H_2O = CO_2 + 4H_2$.

Mechanism (B) consists of 3 routes $N^{(1)}$, $N^{(2)}$, and $N^{(3)}$, each route comprising a single slow step and other steps are quasi equilibria. Under assumption of surface uniformity, the following expressions were derived for the rate of each route:

$$r^{(1)} = \frac{k_1 P_{CH_4} P_{H_2O} [Z]^2}{P_{H_2}^{5/2}} (1 - X_{(1)}) \qquad (6)$$

$$r^{(2)} = \frac{k_2 P_{CO} P_{H_2O} [Z]^2}{P_{H_2}} (1 - X_{(2)}) \qquad (7)$$

$$r^{(3)} = \frac{k_1 P_{CH_4} P_{H_2O}^2 [Z]^2}{P_{H_2}^{7/2}} (1 - X_{(3)}) \qquad (8)$$

where $X_{(1)} = (1/K_{(1)})(P_{CO}P_{H_2}^3 / P_{CH_4}P_{H_2O})$ shows the degree of approach to equilibrium of the reaction according to route $N^{(1)}$, $X_{(2)}$ and $X_{(3)}$ have the similar sense.

The methane consumption rate is

$$-r_{CH_4} = r^{(1)} + r^{(3)} \qquad (9)$$

It is assumed that surface is covered mostly with adsorbed oxygen atoms and molecules of CO, H_2, and CH_4. Then,

$$[Z] = \frac{1}{1 + K_{H_2O}(P_{H_2O}/P_{H_2}) + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{CH_4}P_{CH_4}} \qquad (10)$$

The kinetic model of [7,8] with fitted rate constants succeeded in the description of experimental data on the dependence of methane consumption rate and the rate of carbon dioxide formation on contact time, but failed to describe the rate of carbon monoxide formation. This result was caused by the procedure used by the authors while fitting the rate constants, since as experimental observations methane conversion and carbon dioxide yield were chosen which are very close to each other. We refined the kinetic parameters on the basis of data on methane conversion and carbon monoxide, but not carbon dioxide yield, and thus the drawback of the procedure in [7,8] was overcame.

However, some suppositions of model [B] provoke objections. The theoretical value of the pre-exponential factor $K_{H_2O}^0$, which is derived from the absolute reaction rate theory ($0.162 \cdot T^{-1/2}$) is 8 orders of magnitude higher than that obtained in [3] from the fit of experimental data. This means that the experimental dependence of the reaction rate on the steam partial pressure cannot be explained by a high surface coverage of oxygen atoms. In the models of [7,8] the surface coverage of absorbed methane molecules is also considerable. It seems improbable that methane molecules may firmly bind with the nickel surface without dissociation.

Table 1
Methane conversion with steam and carbon dioxide and P_{CO} at the reactor outlet on Ni-1 and Ni-2.

		650 °C	600 °C	550 °C	500 °C
Ni-1	$CH_4 + H_2O + H_2$ $\quad X_{CH_4}$, %	13.0	8.1	3.65	1.53
	P_{CO}, bar	0.0040	0.0014	0.0002	0
	$CH_4 + CO_2 + H_2$ $\quad X_{CH_4}$, %	10.5	5.8	2.8	0.84
	P_{CO}, bar	0.085	0.061	0.035	0.025
Ni-2	$CH_4 + H_2O + H_2$ $\quad X_{CH_4}$, %	50.2	36.5	23.4	10.6
	P_{CO}, bar	0.020	0.010	0.004	0.0009
	$CH_4 + CO_2 + H_2$ $\quad X_{CH_4}$, %	38.0	24.3	15.5	6.8
	P_{CO}, bar	0.220	0.160	0.120	0.062

1.3. Aparicio model

An investigation aimed to elucidate several elementary surface reactions in methane conversion on nickel catalyst has been made by Aparicio [9] using the isotope exchange method.

Certain data on elementary steps of methane adsorption were obtained by studying the kinetics of isotope exchange between CD_4 and H_2. It was found that the adsorption of methane molecule is accompanied with the dissociation to an adsorbed species CH_3 and an adsorbed H atom. Furthermore, additional hydrogen atoms on the surface detach from methane fragments with the desorption of molecular hydrogen. The mentioned reactions are reversible; hence CD_4 exchanges deuterium with H_2 which results in the formation of molecules containing $CD_{4-x}H_x$, $0 < x < 4$. Activation energies and pre-exponential factors for some elementary steps of hydrogen atom detachment from methane and its fragments have been obtained in [9]. The methane adsorption rate on nickel will be discussed later.

Isotope exchange between H_2O and D_2 molecules was also studied. The exchange proceeds at a high rate at 100–200 °C. Already at these temperatures a reversible dissociative adsorption of water takes place on the surface with the formation of surface H, O and OH. A microkinetic model of methane conversion was proposed which includes a step of OH interaction with C atoms on the surface. However, due to the complexity of the mechanism it was impossible to obtain the kinetic equation in an explicit form. Nevertheless, calculations could describe experimental data [9]. The presently suggested mechanism of methane reforming contains several steps of mechanism [9].

2. Experimental

2.1. Methods of kinetic experiments

Several tests aimed to study the relationship between mechanisms of steam and dry reforming of methane were performed in a plug-flow reactor at atmospheric pressure. The experimental procedure was described in detail in [10].

Two supported nickel catalyst were used:

Ni-1 nickel supported on MgO, nickel content 1.4 wt.%, active nickel surface 1.1 m²/g;
Ni-2 nickel supported on magnesium spinel $MgAl_2O_4$, nickel content 16.0 wt.%, active nickel surface 5.3 m²/g.

The rates of steam and dry methane reforming were compared at catalyst charge 25 mg Ni-1 or Ni-2 (Table 1). In the case of steam methane reforming the reactor was supplied with 4.0 *NL*/h CH_4, 16.0 *NL*/h H_2O, and 1.6 *NL*/h H_2; whereas for dry reforming with 4.0 *NL*/h CH_4; 16.0 *NL*/h CO_2; and 1.6 *NL*/h H_2. These tests were performed at 650, 600, 550, and 500 °C.

The effect of hydrogen on the rate of dry methane reforming was studied at 500 °C in the reactor charged with 50 mg Ni-1.

A.K. Avetisov et al. / Journal of Molecular Catalysis A: Chemical 315 (2010) 155–162

Table 2
Influence of hydrogen on dry methane reforming on Ni-1.

	X_{CH_4}, %	P_{CO} exit, bars
$CH_4 + CO_2$	3.38	0.023
$CH_4 + CO_2 + H_2$	1.90	0.053

The methane conversion was compared for tests with and without hydrogen input into the reactor (Table 2).

The effect of partial pressure of steam on the methane conversion on Ni-1 was studied at 500 °C. For this end, the feed rate of steam into the reactor was decreased, the steam being replaced with nitrogen which is inactive in the reactions.

The study of methane reforming at atmospheric pressure was performed also under gradientless conditions using a circulation flow glass unit. The circulation of gaseous reaction mixture was induced with an electromagnetic circulation pump with a valve unit. The reactor vessel was made of fused silica.

Since the reaction occurs at a considerable steam partial pressure, in order to avoid water condensation on the unit walls, the circulation unit was placed in a heated oven which is maintained at 120–140 °C. Special valves with Teflon gaskets were used without lubricant. For heating gas mixture entering the reactor, the latter was provided with a coil. The reactor was heated with a furnace with fluidized corundum bed to enhance heat transfer to the coil and the reaction vessel.

The flows of the reaction mixture components (pure H_2, CO_2, CH_4, as well as Ar after additional purifications) to the reactor were controlled with a gas flow-meter (Brooks Instrument Model 5850 E). The water flow was set by a liquid flow-meter, and afterwards the water entered the evaporator and the water steam was mixed with other gaseous components of the feed mixture.

Before entering the flow circuit, the gas mixture passes an additional pre-reactor made of fused silica and heated to the predetermined temperature (from 300 up to 600 °C), in which an excess amount (ca. 150 cm^3) of steam methane reforming catalyst was placed. On the one hand, the pre-reactor takes up poison traces of supplied gas mixture. On the other hand, by varying the pre-reactor temperature it is possible to set the desirable composition of the supplied mixture.

The study of methane reforming at elevated pressures (up to 30 bars) was performed in a plug-flow mode. Here the reactor made of copper was used which had the form of a rectangular 2 mm × 12 mm in order to increase heat transfer with the furnace with fluidized corundum bed. It was checked in separate experiments in the absence of the catalyst that the conversion on the reactor sidewalls is negligible.

The analysis of the reaction gas mixture was performed using gas chromatography. As internal standard, argon was used which was fed at a fixed rate together with the reaction mixture.

Two gas chromatographs were used separately (Tsvet 530).

One sample was injected in GC1 with three sequential columns arranged in the following way: column 1 → TCD → adsorber for removing water vapor (molecular sieve 50 nm, 1 = 0.1 m) → empty stainless steel tube with diameter 3 mm and length 12 m and thereafter columns 2 + columns 3 followed by TCD. Column 1 of 3 m length packed with Polysorb 1 (an analogue of Porapak Q) was used for analysis of H_2O at 150 °C. It allowed separation of water from the sum of $H_2 + Ar + CO + CH_4 + CO_2$. Columns 2 (molecular sieve 13X, 1.5 m, room temperature) and 3 (special carbon material PAU-2, 2 m, temperature is (0–(−7))°C) with stainless steel material of tubing were used for analysis of CH_4 and CO. These columns were able to separate H_2, Ar, CO and CH_4. The carrier gas in GC1 was helium.

Another sample was injected in the chromatograph 2 with four columns with stainless steel material of tubing arranged as follows: columns 1 (Porapak Q, 1 m) and 2 (Polysorb 1, 1 m) → TCD → empty

stainless steel tube of diameter 3 mm and length 9 m → columns 3 (molecular sieve 5A, 3 m) and 4 (PAU-2, 2 m → TCD]. The carrier gas was nitrogen. In GC2 columns 1 and 2 were applied for analysis of CO_2 at the room temperature. These columns separated the peak of sum ($H_2 + Ar$), the peak of CH_4 and the peak of CO_2. Columns 3 and 4 operating also at room temperature were utilized for analysis of H_2 and separated H_2, Ar and CH_4.

The information from both GC were processed using the software "ChromProcessor".

The samples of gas for chromatographic analysis may be taken from the flow circuit inlet and outlet. The difference between flows of each reaction participant divided to the weight of catalyst and time gave the average reaction rate with respect to this component.

2.2. Model parameter fitting

The modeling according to the derived kinetic equations was realized as follows. The inverse kinetic problems to evaluate kinetic parameters were solved by minimizing sums of squares of relative deviations of experimental and calculated values of methane conversion and carbon oxides yields (for experiments in plug-flow reactors) and the rates of formation or consumption of key substances, i.e. methane and carbon dioxide (for experiments in a circulation flow reactor). The Fick's model was used in the calculations of reaction rates on catalyst grains of known size in order to take into account the diffusion inside pores. The apparent diffusion coefficient was calculated on the basis of known pore volume distribution in pore radius and from experimental values of diffusion permeability. The detail of mathematical model and calculation methods are given in [11].

3. Results and discussion

3.1. Results of experiments

Table 1 presents methane conversion, X_{CH_4}, and carbon monoxide partial pressure, P_{CO}, at the plug-flow reactor outlet for steam and dry reforming. As can be seen from Table 1 in the case of dry reforming on Ni-2, P_{CO} at the reactor outlet is significantly higher than P_{CO} at the reactor outlet for dry reforming on Ni-1 and P_{CO} at the reactor outlet for steam reforming on both catalysts.

The data given in Table 1 gives the possibility to assume that the decrease in X_{CH_4} in dry reforming over Ni-2 is due to a significant Ni-2 surface coverage with carbon monoxide.

Additionally some experiments on methane reforming at 500 °C on Ni-1catalyst were performed in order to check the effect of hydrogen addition to the $CH_4 + CO_2$ mixture. The results are given in Table 2.

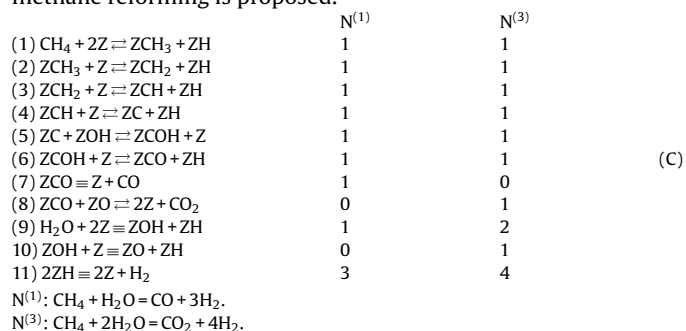### 3.2. Modified microkinetic model of methane steam and dry reforming

As was indicated above, the experiments by Froment and Xu [7,8] have shown, that kinetic features of methane conversion at pressures up to 15 bars are similar to the features obtained in [3]. Namely, the reaction is accelerated by steam and decelerated by hydrogen. It is natural to accept that the reason of these effects is the same as proposed in [3].

A new peculiarity observed in experiments of [7,8] was the decrease in the reaction order with respect to methane: it is lower than unity. This may be explained by the fact that at elevated methane pressures its adsorbed fragments occupy a significant part of the surface.

According to [9], methane adsorbs on the nickel surface with the dissociation into an adsorbed hydrogen atom and an adsorbed

methane fragment, CH_3. Then CH_3 species dissociates on the surface, etc. Such a mechanism of adsorption may be taken into account in the kinetic model of methane reforming. Similarly, the result of [9] may be included in the model; namely that water molecules also adsorb with the dissociation into adsorbed OH, O, and H, which are in equilibrium with water and hydrogen from the gas phase. The step of the interaction of adsorbed carbon monoxide and adsorbed oxygen atom resulted in the formation of carbon dioxide should also be included in the model.

With all this taken into account, the following kinetic model of methane reforming is proposed.

	$N^{(1)}$	$N^{(3)}$
(1) $CH_4 + 2Z \rightleftarrows ZCH_3 + ZH$	1	1
(2) $ZCH_3 + Z \rightleftarrows ZCH_2 + ZH$	1	1
(3) $ZCH_2 + Z \rightleftarrows ZCH + ZH$	1	1
(4) $ZCH + Z \rightleftarrows ZC + ZH$	1	1
(5) $ZC + ZOH \rightleftarrows ZCOH + Z$	1	1
(6) $ZCOH + Z \rightleftarrows ZCO + ZH$	1	1
(7) $ZCO \rightleftharpoons Z + CO$	1	0
(8) $ZCO + ZO \rightleftarrows 2Z + CO_2$	0	1
(9) $H_2O + 2Z \rightleftharpoons ZOH + ZH$	1	2
10) $ZOH + Z \rightleftharpoons ZO + ZH$	0	1
11) $2ZH \rightleftharpoons 2Z + H_2$	3	4

(C)

$N^{(1)}$: $CH_4 + H_2O = CO + 3H_2$.
$N^{(3)}$: $CH_4 + 2H_2O = CO_2 + 4H_2$.

$$r_{CH_4} = -\frac{k_1 P_{CH_4}(1-(1/K_{(1)})(P_{H_2}^3 P_{CO}/P_{H_2}P_{CH_4})(1+(k_{-8}/k_{-7})(P_{CO_2}/P_{CO})[Z]/1+(k_{-8}/k_{-7})K_{(2)}(P_{H_2O}/P_{H_2})[Z]))}{(1+A_4(P_{H_2}^{5/2}/P_{H_2O}))[1+K_{CH_3}(P_{CH_4}/P_{H_2}^{1/2})(1-((1-X)/1+A_4(P_{H_2}^{5/2}/P_{H_2O})))+K_{CO}P_{CO}]^2},$$

(16)

It is assumed that each adsorbed species requires a single adsorption site. It is supposed also that surface concentrations of all species except for ZCH_3 and ZCO are low. The, mechanism (C) results in the following equations for the reaction rates for the key components, i.e. methane and carbon dioxide:

$$-r_{CH_4} = r^{(1)} + r^{(3)} = \frac{k_1 P_{CH_4}(1-X)[Z]^2}{DEN}$$

(11)

$$r_{CO_2} = r^{(3)} = \frac{NUM}{1+(k_{-8}/k_{-7})K_{(2)}(P_{H_2O}/P_{H_2})[Z]}$$

(12)

where

$$NUM = -r_{CH_4}\frac{k_{-8}}{k_{-7}}K_{(2)}\frac{P_{H_2O}}{P_{H_2}}[Z] - k_{-8}\left(P_{CO_2} - K_{(2)}\frac{P_{CO}P_{H_2O}}{P_{H_2}}\right)[Z]^2,$$

$$DEN = 1 + A_1 P_{H_2}^{1/2} + A_2 P_{H_2} + A_3 P_{H_2}^{3/2} + A_4\frac{P_{H_2}^{5/2}}{P_{H_2O}}$$

$$+ A_5 \frac{P_{H_2}^3[Z]}{P_{H_2O}(1+(k_{-8}/k_{-7})K_{(2)}(P_{H_2O}/P_{H_2})[Z])}.$$

(13)

$$A_1 = \frac{k_{-1}}{k_2}K_{-11}^{1/2}, \quad A_2 = \frac{k_{-1}k_{-2}}{k_2k_3}K_{-11}, \quad A_3 = \frac{k_{-1}k_{-2}k_{-3}}{k_2k_3k_4}K_{-11}^{3/2},$$

$$A_4 = \frac{k_{-1}k_{-2}k_{-3}k_{-4}}{k_2k_3k_4K_9}\left(1+\frac{k_{-5}}{k_6}\right)K_{-11}^{5/2}, \quad A_5 = \frac{k_1}{K_{(I)}k_{-7}},$$

$$X = \frac{1}{K_{(1)}}\frac{P_{H_2}^3 P_{CO}}{P_{H_2O}P_{CH_4}}\frac{1+(k_{-8}/k_{-7})(P_{CO_2}/P_{CO})[Z]}{1+(k_{-8}/k_{-7})K_{(2)}(P_{H_2O}/P_{H_2})[Z]}.$$

Equating expression (11) to the rate of the first step, one obtains

$$[ZCH_3] = \frac{k_1 P_{CH_4}}{k_{-1}K_{-11}^{1/2}P_{H_2}^{1/2}}[Z]\left(1-\frac{(1-X)}{DEN}\right)$$

$$= K_{CH_3}\frac{P_{CH_4}}{P_{H_2}^{1/2}}[Z]\left(1-\frac{(1-X)}{DEN}\right).$$

(14)

Taking into account equilibrium of step 7, we obtain the expression for the fraction of non-occupied surface [Z]:

$$[Z] = \frac{1}{1+K_{CH_3}(P_{CH_4}/P_{H_2}^{1/2})(1-((1-X)/DEN))+K_{CO}P_{CO}}$$

(15)

where $K_{CO} = k_{-7}/k_7$

If the adsorption rates of carbon monoxide and carbon dioxide are much higher than the methane adsorption rate (and this follows from the data given in [9]), the term with A_5 in DEN may be neglected. Let us assume also that A_1, A_2 and A_3 are much lower than unity. Then, the Eq. (11) converts into

where $K_{CO} = k_{-7}/k_7$.

When the water gas-shift reaction (reaction (2) is in equilibrium, $X = X_{(1)}$. This condition is valid in almost all analyzed kinetic experiments on steam methane reforming, therefore Eq. (16) is sufficient for their description. For the same reason it is impossible to extract k_{-7} and k_{-8} from these experiments because they enter Eq. (16) as ratio.

In the experiments on dry methane reforming the equilibrium of reaction (2) was not reached. Since the partial pressure of carbon dioxide is much higher under these conditions than the partial pressure of steam, it may be assumed that CO_2 adsorption is at quasi-equilibrium whereas either step leading to the H_2O absorption (i.e. step 9 or 10) becomes non-equilibrium. For such a case the following relationships were obtained

$$-r_{CO_2} = k_{-9}\frac{K_{-8}K_{-10}K_{-11}}{K_{-7}}\frac{P_{H_2}P_{CO_2}}{P_{CO}}[Z]^2\left(1-K_{(2)}\frac{P_{H_2O}P_{CO}}{P_{CO_2}P_{H_2}}\right) - r_{CH_4}$$

$$= k'_{CO_2}\frac{P_{H_2}P_{CO_2}}{P_{CO}}[Z]^2\left(1-K_{(2)}\frac{P_{H_2O}P_{CO}}{P_{CO_2}P_{H_2}}\right) - r_{CH_4}$$

(17)

$$-r_{CO_2} = k_{-10}\frac{K_{-8}K_{-11}^{1/2}}{K_{-7}}\frac{P_{H_2}^{1/2}P_{CO_2}}{P_{CO}}[Z]^2\left(1-K_{(2)}\frac{P_{H_2O}P_{CO}}{P_{CO_2}P_{H_2}}\right)$$

$$= k_{CO_2}\frac{P_{H_2}^{1/2}P_{CO_2}}{P_{CO}}[Z]^2\left(1-K_{(2)}\frac{P_{H_2O}P_{CO}}{P_{CO_2}P_{H_2}}\right)$$

(18)

Modeling of the data obtained in a plug-flow reactor at atmospheric pressure was performed as follows. First, from the experiments on steam methane reforming on Ni-1 pre-exponential factors and activation energy of the rate constant, k_1, were estimated considering that [Z] = 1, DEN = 1 in Eq. (11), and $r_{CH_4} = k_1 P_{CH_4}$ (the dimension of reaction rates is mole/(g(cat)·h), and partial pressures are expressed in bars). Next, from the ratio of specific nickel surfaces of Ni-2 and Ni-1, the pre-exponential factor of k_1 was increased five fold and the validity of the obtained kinetic parameters was examined in the experiments on steam methane reforming
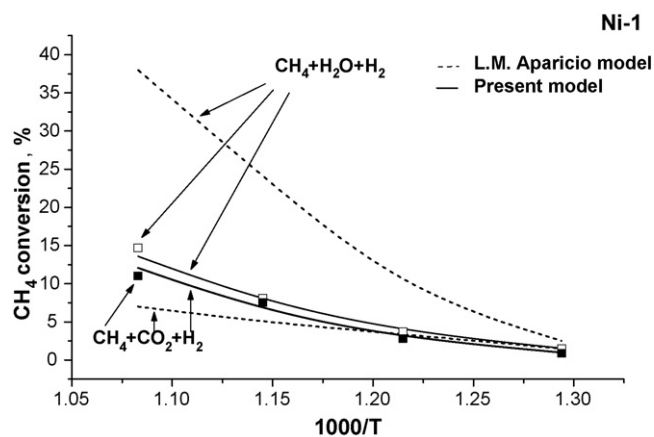
Fig. 1. Experimental (points) and calculated (lines) CH_4 conversions in steam and carbon dioxide methane reforming on Ni-1 (according to the present model and model in [9]).

Fig. 3. Dependence of methane reforming rate on the ratio partial pressures of hydrogen and steam.

on Ni-2. The following dependence was found for this catalyst sample: $\ln k_1 = 17.4 - 12{,}000/T$.

Then, the experiments on steam and dry methane reforming on Ni-2 were treated together by assuming that $[Z] = 1/(1 + K_{CO}P_{CO})$ and $DEN = 1$ in Eq. (11). The following expressions $\ln k'_{CO_2} = 10, 0\text{-}6000/T$, $\ln k_{CO_2} = 9, 5\text{-}6000/T$ $k_{-8}/k_{-7} \approx 1$, and $\ln K_{CO} = -13{,}4 + 11{,}400/T$ were obtained. Thereafter the found values of the pre-exponential factors of k'_{CO_2} and k_{CO_2} were decreased according to the ratio of specific surfaces on Ni-2 and Ni-1 (i.e. by 5 times) and the parameters thus obtained were checked in the experiments on dry methane reforming on Ni-1. The results of modeling are shown in Figs. 1 and 2. As can be seen, the proposed model is in much better agreement with the data obtained in the flow reactor, than the model [9].

Our calculations show that the experiments both on Ni-2 and Ni-1 proceeded in the region of pore-diffusion resistance. Thus, on Ni-2 the efficiency for dry reforming was varied from $\eta(CH_4) = 0.341$ and $\eta(CO) = 0.196$ at $T = 650\,^\circ C$ to $\eta(CH_4) = 0.664$ and $\eta(CO) = 0.258$ at $T = 500\,^\circ C$, and on Ni-1 from $\eta(CH_4) = 0.708$ and $\eta(CO) = 0.398$ at $T = 650\,^\circ C$ to $\eta(CH_4) = 0.797$ and $\eta(CO) = 0.380$ at $T = 500\,^\circ C$.

For the estimation of parameter A_4 in Eq. (16), a set of data (see Fig. 3) obtained in a circulation flow unit was used wherein the ratio $(P_{H_2}^{5/2}/P_{H_2O})$ was varied within a broad range. The fitting with the use of K_{CO} obtained above shows that $K_{CO}P_{CO} \ll 1$ in these experiments.

Furthermore, taking into account that the rate is of the first-order in methane at ambient pressure, so that $K_{CH_3}(P_{CH_4}/P_{H_2}^{1/2})$ is also negligible in comparison with unity and $[Z] \approx 1$. In this case, Eq. (16) may be linearized as shown in Fig. 3 in corresponding coordinates. Fig. 3 demonstrates the dependence of methane reforming rate on the ratio of hydrogen and water partial pressures.

Fitting k_1, k'_{CO_2}, k_{CO_2}, and K_{CO} for the whole set of experimental data gives the following value for $A_4 = \exp(-8.53 + 8000/T)$.

The results shown in Fig. 4 illustrate that the k_1 temperature dependence is valid for the experiments performed both in circulation flow unit and plug-flow reactors at atmospheric pressure.

For the estimation of K_{CH_3}, the data of [7] specified in [8] were used. As an objective function, the sum of squares of relative deviations between experimental and calculated values for methane conversion and carbon monoxide yield were used. All parameters entering Eq. (16) were fixed except for K_{CH_3}. In total, 195 experimental data points for methane conversion and carbon monoxide yield were used, the latter being calculated as the difference between methane conversion and carbon dioxide yield indicated in [8]. It was obtained that $K_{CH_3} = \exp(-5.72 - 4820/T)$
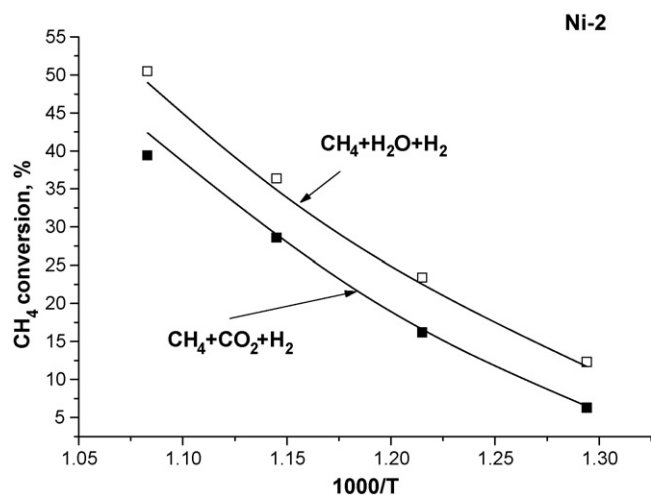

Fig. 2. Agreement between experimental and calculated (the present model) data on steam and carbon dioxide methane reforming on Ni-2 catalyst.
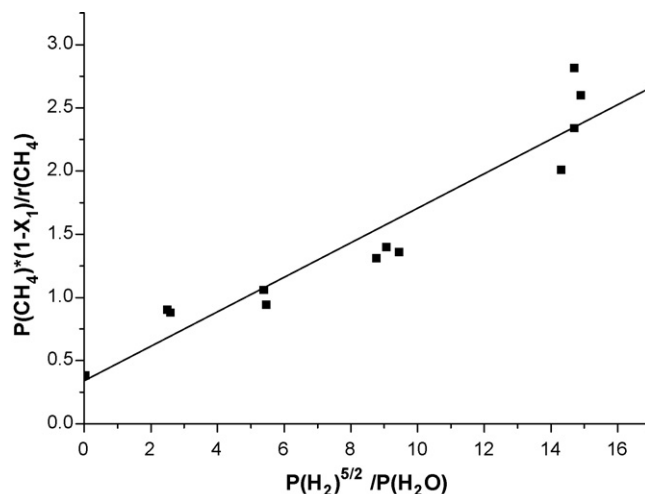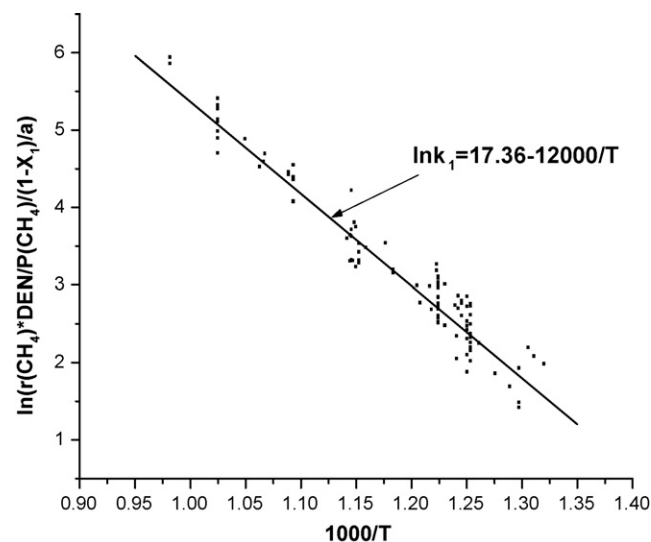

Fig. 4. Dependence of k_1 on $1/T$ extracted from the experiments in the circulation flow unit (a is the activity coefficient of the catalyst, the water gas shift reaction is in equilibrium).

3.3. Analysis of pre-exponential factors

Thus, modeling kinetics of methane steam and dry reforming according to Eqs. (16)–(18) enables us to evaluate the rate constants k_1, k'_{CO_2}, k_{CO_2}, the ratio k_{-8}/k_{-7} and parameters A_4, K_{CH_3}, and K_{CO}. Let us analyze the correspondence of the obtained preexponential factors (i.e. experimental values) to the absolute reaction rate theory which for heterogeneous processes was developed for the first time by Temkin [12] (for more recent account of the theory see [13]). It is usually believed that the differences between these quantities within the limits of one order of magnitude are admissible and confirming the assumptions made at a formulation of kinetic model.

A good estimation for the pre-exponents of the rate constants of adsorption is the number of collisions of molecules with the catalyst surface [13]:

$$\nu = 2.635 \times 10^{25} \frac{P}{\sqrt{MT}}, \tag{19}$$

where M is the molar mass, P is the pressure (in bar), T is the absolute temperature; the dimension of ν being molecules cm^{-2} s^{-1}.

Substituting in (19) $P = 1$ bar, corresponding molecular weighs and $T = 873$ K, one obtains $\nu_{CH_4} = 2.2 \times 10^{23}$, $\nu_{CO_2} = 1.32 \times 10^{23}$, $\nu_{H_2} = 6.2 \times 10^{23}$, $\nu_{H_2O} = 2.07 \times 10^{23}$, and $\nu_{CO} = 1.66 \times 10^{23}$ molecules cm^{-2} s^{-1} bar^{-1}. The estimated experimental value $k_1^0 = 10^{23}$ molecules cm^{-2} s^{-1} bar^{-1} agrees well with the estimate above (for the specific nickel surface 5.3 m^2 g$_{(cat)}^{-1}$ and the number of active sites per cm^2 Ni equal to 2×10^{15}, the recalculation coefficient γ for the transition from mole g$_{(cat)}^{-1}$ h^{-1} bar^{-1} to molecules cm^{-2} s^{-1} bar^{-1} is $10^{15.2}$, and that for the transition to molecules site^{-1} s^{-1} bar^{-1}, γ' is 1.5). It should be mentioned that close values $10^{22.8}$ and $10^{22.5}$ molecules cm^{-2} s^{-1} bar^{-1} have been obtained in [9] and [6], respectively (in recalculation the number of sites per cm^2 Ni was also taken equal to 2×10^{15}). As follows from the estimations according to Eq. (19), the ratio $k_{-8}/k_{-7} \approx 1$ at all temperatures. This is why k_{-8}^0/k_{-7}^0 is close to unity irrespective of the adsorption type (dissociative or not), which agrees well with the results of modeling.

For the evaluation of pre-exponential factors of absorption coefficients, let us first use the Temkin's equation [14]:

$$K_j^0 = \frac{1}{T^{1.75} \cdot 10^i}, \tag{20}$$

where i is equal to 3 for molecular adsorption and 1.5 for atomic adsorption. The presently obtained value $K_{CO}^0 = 10^{-5.8}$ bar^{-1} may be considered as only fairly agreeing with the value $10^{-8.15}$ estimated by Eq. (20) ($T = 873$ K was used as an average temperature within the studied region). For the case of localized adsorption, the value of K_{CO}^0 was calculated from the data of [9] as the ratio of pre-exponential factors of the rate constants of CO adsorption and desorption, the value $10^{-4.7}$ bar^{-1} was obtained which is much closer to the experimental value.

To compare theoretical and experimental values of $K_{CH_3}^0$, the estimates of K_{-11}^0 and K_1^0 are necessary. The calculation of these parameters according to expression (20) for dissociative absorption of methane and hydrogen gives for the both parameters the same value $10^{-6.64}$. From here follows that $K_{CH_3}^0 = 10^{-3.32}$ bar$^{-1/2}$, which is approximately one order of magnitude higher than the value $10^{-2.5}$ bar$^{-1/2}$ resulting from modeling. For non-localized adsorption, $K_{-11}^0 = 10^{-4.53}$ bar^{-1} and $K_1^0 = 10^{-3.21}$ bar^{-1}. From here follows that $K_{CH_3}^0 = 10^{-0.94}$ bar$^{-1/2}$ which is somewhat closer to the experimental value.

For further estimations of pre-exponential factors let us suppose, according to [9]: $k_{-1}^0 = 10^{10.4}$, $k_6^0 = 10^{13}$, $k_{-9}^0 = k_{-10}^0 = \cdot 10^{11.5}$

(all in molecules site^{-1} s^{-1}) $K_2^0 = K_3^0 = K_4^0 = 5$, $K_{-5}^0 = 0.2$, $K_{10}^0 = 5$ (the values of the last two were considered by analogy to dissociation steps on the surface, for example, analogously to K_2^0), $K_9^0 = 10^{-10.2}$ bar^{-1}, $K_{-11}^0 = 10^{-4.53}$ bar^{-1}. The ratio K_{-8}^0/K_{-7}^0 was taken as $10^{1.5}$ according to (20).

The expression for A_4 is rather complicated. In the general case, it cannot be represented as Arrhenius equation. However, if the ratio of rate constants of k_{-5} and k_6 is much higher or, to the contrary, much less than unity this expression is simlified and may be represented as Arrhenius equation. Taking into account that in scheme (C) step 5 in the reverse direction and step 6 in the right direction are of similar character, it may be assumed that the ratio of their pre-exponential factors is close to unity. Then, the relationship between these constants is defined by the difference of activation energies of these steps. Let us note that both species in the left-hand side of step 5 behave like radicals and their binding energies with the surface are higher than for the species in the right-hand side of step 6. Then, according to the Evans-Polanyi correlation [12], one may expect that $E_{-5} < E_6$ and $k_{-5}/k_6 > 1$. Hence, $A_4 \cong (k_{-1}k_{-2}k_{-3}k_{-4}/k_2k_3k_4k_5K_9)(k_{-5}/k_6)K_{-11}^{5/2} \cong k_{-1}(K_{-11}^{5/2}/k_6K_2K_3K_4K_5K_9)$. From this it follows that $A_4^0 = 10^{-4.72}$ bar$^{1.5}$, which substantially coincides with the experimental value ($10^{-3.7}$ bar$^{1.5}$).

For the correct choice between Eqs. (17) and (18), both describing the rate of carbon dioxide formation for methane dry reforming let us evaluate the pre-exponential factors of k'_{CO_2} and k_{CO_2} under conditions when water gas-shift reaction is far from equilibrium. The calculations using the values above give $k_{CO_2}^0 = 10^{10.75}$ molecules site^{-1} s^{-1} bar$^{-0.5}$, or $10^{10.58}$ mole g$_{(cat)}^{-1}$ h^{-1} bar$^{-0.5}$, and $k'^0_{CO_2} = 10^{7.76}$ molecules site^{-1} s^{-1} bar^{-1}, or $10^{7.60}$ mole g$_{(cat)}^{-1}$ h^{-1} bar^{-1}. As can be seen, the second value is more closer to the parameter extracted from the kinetic values ($10^{4.34}$ mole g$_{(cat)}^{-1}$ h^{-1} bar^{-1}), which makes the assumptions made while deriving Eq. (18) more plausible.

Thus, the analysis of "experimental" values of pre-exponential factors of the constants entering into the kinetic equations shows that they will correspond well enough with the estimations made on the basis of the transition-state theory. It, in turn, proves the assumptions made at a formulation of the mechanism (C) and at a derivation of the kinetic Eqs. (16)–(18).

Finally we want to make some general comments about applicability of microkinetic analysis to heterogeneous catalytic kinetics of complex multi-step reactions. Kinetics of methane steam reforming under certain conditions can be described by the first order in methane, which within the framework of the mechanisms discussed above, corresponds to the dissociative adsorption of methane as the rate-limiting step. Hereinafter activation energies are indicated in terms of E/R. In Ref. [6] for the conditions of the first order in methane the value of E/R is equal to 12,300–12,600 K. In the present study, for a supported nickel catalyst this value is 12,000 K. It is interesting to note that the activation energy for methane dissociation indicated in [9] for a supported nickel catalyst is 6500 K. This value was obtained from isotope exchange between D_2 and CH_4 between 350 and 450 °C in the absence of any reactants containing oxygen, in particular H_2O and CO_2. Pre-exponential factors in all these three studies are close to each other, it means in fact the rate constant in [9] is substantially higher than in the other works. According to the model of Aparicio [9] there is a large difference between dry and steam reforming of methane, which is most probably connected with an overestimated value [9] of heat of CO chemisorption.

This indicates an apparent danger of direct application of microkinetic methodology to the determination of rate constants from experimental data generated under conditions (temperature,

gas composition, pressure, materials) far from the catalytic ones. On the other hand such data greatly helps to formulate the plausible multi-step reaction mechanism under conditions of real catalysis.

4. Conclusion

The microkinetic model of steam and dry reforming of methane is proposed. In the advanced model the intermediate ZCH_3, of surface coverage which can be significant, is not in equilibrium with components of gas phase CH_4 and H_2. Its inclusion in kinetic model allows describing change of the order of methane rate with varying total pressure. Influence of water and hydrogen on the rate of methane reforming in a forward direction is caused by their influence on reversibility of a step.

Under some conditions (sufficiently large ratio P_{H_2O}/P_{H_2}) the rate of methane reforming is described by the equation of the first order on methane. The same result has been reported in [3,6]. At dry methane reforming there can be significant surface coverage of carbon monoxide. This result explains the reason for the rate of dry methane reforming being less than the rate of steam methane reforming.

In our model the surface coverage of the catalyst with the adsorbed atoms of oxygen, unlike in the model of Xu and Froment, is neglectably small.

Kinetic parameters of the model are adjusted by means of mathematical modeling with the use of own and published [7,8] experimental data. Pore-diffusion resistance was taken into account during calculations. The obtained values of kinetic parameters agree with the estimates obtained according to the transition-state theory.

To summarize, it may be stated that the proposed microkinetic model fairly well describes both published and own experimental data obtained in gradientless and plug-flog systems.

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