

KINETICS OF METHANE CONVERSION OVER MICROSPHERICALLY GRAINED
NICKEL-ALUMINA CATALYSTS

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Kinetics of methane conversion in a fluidized bed of microspherically grained nickel-alumina catalyst has been studied at pressures from 0.3 to 3.1 MPa. The rate equation shows that the reaction is inhibited by H₂O.

Изучена кинетика конверсии метана с водяным паром в кипящем слое микросферического алюмоникелевого катализатора при давлении от 0,3 до 3,1 МПа. Предложено уравнение скорости реакции, по которому конверсия тормозится водяным паром.

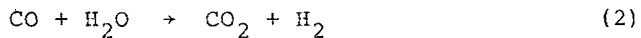
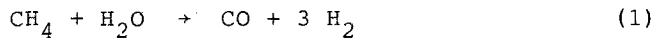
At present hydrogen is largely produced by the conversion of natural gas with H₂O in tubular furnaces. The process efficiency can be essentially increased by using a fluidized catalyst bed with a solid circulating absorbent of CO₂ [1]. The aim of the present study was to examine the kinetics of methane conversion in the fluidized bed of microspherically grained nickel-alumina catalyst that can be used in processes with CO₂ absorption.

Experimental conditions were chosen with taking into account the results of thermodynamic analysis [2], showing that the absorption of CO₂ decreases the reaction temperature and permits to carry out the process at sufficiently high pressures.

The reaction was studied at temperatures from 520 to 720 °C and pressures from 0.3 to 3.1 MPa, at a H₂O : CH₄ mole ratio of 4:1. Space velocity of methane ranged from 5000 to 30.000 h⁻¹.

Catalysts were prepared by impregnating microspherically γ-Al₂O₃ from the solution of nickel nitrate. Samples were calcined at 1000 °C for 4 h and then reduced by hydrogen at 800 °C and 1.0 MPa for 4 h. Surface areas of catalysts were 96-99 m²/g and the bulk density 0.75-0.88 g/cm³. Average diameter of catalyst grains was 250 μm.

The diameter of the reactor charged with 1.2-16.0 g catalyst was 30 mm. All experiments were carried out at a linear gas flow velocity of about 0.1 m/s. Concentrations of H₂, CO, CO₂ and CH₄ in the converted gas were determined chromatographically. Methane conversion X was calculated from the data on gas composition and compared with its equilibrium value X^x. The latter was calculated for the reactions



Equilibrium constants were taken from Ref. [3].

Experimental conditions and results are given in Tables 1 and 2.

Various equations for the reaction rate were proposed in Refs [4-6]. We took the equation from Ref. [5] as the initial one

$$r = k(P_{\text{CH}_4}) - P_{\text{CH}_4}^x \quad (3)$$

where r is the reaction rate and P_{CH₄} and P_{CH₄}^x are partial and equilibrium partial pressures of methane.

This equation, however, proved to be unacceptable for the experimental conditions from Table 2: eq. 3 implies that the ratio X/X^x at the same space velocity V₀ should grow with increasing P₀, but in our experiments X/X^x was approximately constant irrespective of P₀.

Table 1
 CH_4 conversion over catalysts with various contents of
 NiO at 2.1 MPa

NiO (wt.%)	5.1		7.7		12.4		12.4
T (K)	893		893		893		793
V_o (h^{-1})	30000	19000	30000	19000	30000	25000	18000
x	0.14	0.19	0.17	0.24	0.22	0.24	0.11
X/X^*	0.38	0.52	0.46	0.65	0.60	0.66	0.60
k (MPa/s)	4.11	3.90	5.28	5.28	7.95	8.03	2.95

Table 2
 CH_4 conversion at various temperatures and pressures
 over 12.4% NiO catalyst

T (K)	893				
V_o (h^{-1})	19600	19600	19600	18000	19600
P_o (MPa)	0.3	0.6	1.1	2.1	3.1
X	0.56	0.45	0.38	0.28	0.26
X/X^*	0.79	0.79	0.80	0.81	0.80
k (MPa/s)	8.53	8.36	9.09	8.16	9.05
T (K)	993				
V_o (h^{-1})	19600	19600	19600	17000	19600
P_o (MPa)	0.3	0.6	1.1	2.1	3.1
X	0.80	0.76	0.66	0.55	0.48
X/X^*	0.84	0.84	0.86	0.89	0.85
k (MPa/s)	11.5	13.2	13.3	12.2	13.9

Table 2 shows the reaction inhibition effect not accounted for in eq. 3. The authors of Ref. [6] described their results using an equation implying that the reaction is inhibited by hydrogen and its rate is inversely proportional to the partial pressure of hydrogen. We tested the similar equation

$$r = k (P_{\text{CH}_4} - P_{\text{CH}_4}^*) / P_{\text{H}_2} \quad (4)$$

but our experimental data have not confirmed it.

Our results can be described assuming that the reaction is inhibited by H_2O

$$r = k (P_{\text{CH}_4} - P_{\text{CH}_4}^*) / P_{\text{H}_2\text{O}} \quad (5)$$

The equation for the reaction rate in a plug flow reactor corresponding to eq. 5 will be

$$\frac{dx}{dz} = \frac{k (1 - \epsilon) F (1 + m)}{W_0 P_0} \frac{(P_{\text{CH}_4} - P_{\text{CH}_4}^*)}{P_{\text{H}_2\text{O}}} \quad (6)$$

where the reaction rate r is referred to unit volume of catalyst, z is the coordinate, W_0 is the volume of gas introduced into the reactor for a certain period of time, m is the $\text{H}_2\text{O}:\text{CH}_4$ mole ratio in the initial mixture, ϵ is the bed porosity and F is the reactor cross section.

After integration, eq. 6 gives

$$k = \frac{P_0}{\tau (1 + m)} \int_0^X \frac{P_{\text{CH}_4} - P_{\text{CH}_4}^*}{P_{\text{H}_2\text{O}}} dx \quad (7)$$

where $\tau = \frac{(1 - \epsilon) L F}{W_0} = \frac{1}{q V_0 (1 + m)}$ is the contact time, L is the bed height and q is the ratio of volumes occupied by 1 mol gas under experimental and normal conditions. Stoichiometric equations 1 and 2 can be used to determine the gas composition as a function of two variables x and β , where β is a part of methane converted into carbon monoxide. Reaction 2 over nickel catalysts is, however, fast [4] and β can be determined as a function of x from the equilibrium equation for this reac-

tion. Thus, the well-known functions of x in eq. 7 are under the integral: therefore, after calculating the integral and knowing values of V_o , P_o and x the constant k can be determined.

Experimental data obtained at 2.1 MPa over catalyst samples with various contents of the active component are represented in Table 1. As is seen from Table 1, with varying space velocities the value of k remains approximately unchanged in accordance with eq. 5. Besides, it is possible to confirm that in the fluidized bed reactor under our experimental conditions gas flow is close to ideal displacement.

Constant k rises with the concentration of active component (Table 1). The ratio of k to nickel concentration slightly decreases with increasing NiO content. But this decrease is relatively small and one can suggest that the surface coverage of the carrier with the active component is close to monolayer for the samples studied.

As is seen from Table 2, k remains approximately unchanged after a more than tenfold change of pressure in the system and its average deviation equals 5%. Thus, eq. 3 is confirmed by the results of all of our experiments.

Activation energy (Tables 1 and 2) for 12.4% NiO catalyst is 50 kJ/mol. Calculations show that the part of the accessible catalyst surface is below 7%, i.e. the reaction takes place in the diffusion regime.

A mechanism of methane conversion implying that the reaction occurs on one active site of the catalyst to form first a chemisorbed particle $=CH_2$, then $-CHOH$, etc., was suggested in Ref. [4]. Rate equations corresponding to this mechanism cannot be coordinated with our experimental data. It is likely that there exists some other mechanism in accordance with which the the reaction takes place on two sites of catalyst occupied by adsorbed molecules of CH_4 and H_2O . Let us suppose that the catalyst surface is homogeneous, the reaction rate is proportional to the surface concentrations of CH_4 and H_2O , adsorption equilibrium is quickly set up on the surface and the reverse reaction can be ignored. If the surface is occupied almost completely by

adsorbed molecules of H_2O , than the reaction rate should be proportional to P_{CH_4} and inversely proportional to P_{H_2O} in accordance with eq. 5⁴ for $P_{CH_4} \gg P_{CH_4}^*$.

Equations 5 and 3 are empirical and our experimental data are insufficient to elucidate the mechanism of ethane conversion on the samples studied. It is clear that these equations do not contradict the hypothesis that the reaction occurs on two active sites of the catalyst.

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