Kinetics of Partial Methane Oxidation Process over the Fe-ZSM-5 Catalysts*

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Kinetics of a partial methane oxidation over the Fe-ZSM-5 catalysts was investigated. A set of rate equations describing the reaction system was suggested and verified by comparison with experimental data. It was found that all the reactions considered were of the zero order with respect to oxygen and of the first order with respect to the oxidized species (methane, methanol, or formaldehyde). Values of the reaction rate constant for the temperature range 350—550 °C as well as the reaction apparent activation energy values were determined.

The studies on the process of partial methane oxidation conducted over the Fe-ZSM-5 catalysts confirmed the assumption that methanol and carbon dioxide are the primary products of the reaction. As a result of the methanol oxidation, formaldehyde is generated, the oxidation of which leads to receiving slight quantities of CO_2.

The decline of the iron content results in the decrease of the rate of every reaction. In order to impede the oxidation of methanol to formaldehyde, the H catalysts should be employed. This form is responsible for the production of methanol; yet it also leads to the direct methane to carbon dioxide oxidation. Bearing such dependences in mind, it could be concluded that the introduction of the Fe-ZSM-5 catalyst demonstrating certain content might result in a favoured reaction of synthesis of methanol, with the process of its further oxidation being hampered. Unfortunately, this makes the elimination of the reaction of oxidation to CO_2 virtually impossible.

It is also evident that the activation energy of methane to methanol or carbon dioxide oxidation is markedly higher than the activation energy of the unwelcome reactions, which are methanol and formaldehyde oxidations.

Studies regarding the process of direct methane oxidation to oxidation products different from those obtained when preparing synthesis gas were conducted already at the beginning of the 20th century [1]. However, finding of a catalyst allowing obtaining methanol or formaldehyde with a satisfactory yield was found to be quite complicated task. Since, methane combustion to carbon oxides is thermodynamically favoured, formaldehyde or methanol synthesis by direct methane oxidation, although thermodynamically feasible, is less probable. The most complicated is the direct methanol production.

Number of catalysts showing different composition and structure were examined over the last century [2]. It was found that carbon oxides and formaldehyde are the principal products of methane oxidation with oxygen [3—9]. If nitric oxide N_2O was used to oxidize methane, higher portion of formaldehyde was obtained and also methanol production was possible [10—13]. Until now, the highest yield of formaldehyde was obtained when molybdenum and vanadium compounds supported on silica were applied [5—8]. Unfortunately, selectivity of methane oxidation to formaldehyde never exceeded 10 %, *i.e.* highly active catalysts demonstrated low selectivity towards products of partial methane oxidation, and highly selective catalysts showed extremely low activity. Despite this fact literature offers a few examples of catalysts that allow production of methanol by a direct methane oxidation with oxygen, *e.g.* Fe-sodalite [14], ZSM-5 [15], Fe-ZSM-5 [16]. Methanol, formaldehyde, and carbon dioxide are the main products of methane oxidation carried out with the use of this catalyst.

The aim of this paper was to investigate kinetics of the process of partial methane oxidation in the presence of Fe-ZSM-5 catalysts, containing iron and silicon in their framework only.

EXPERIMENTAL

Metallosilicates with the ZSM-5 structure were used as catalysts with atomic ratio $n(\text{Si}) : n(\text{Fe})$ of 45, 34, and 22. Both forms, H-ZSM-5 and Na-ZSM-5, were used for the catalyst preparation. Catalyst preparation, apparatus, in which the catalysts were prepared, as well as analysis of the reaction mixture was described in [16].

The reaction was carried out in the vertical flow reactor containing a catalyst. Methane and oxygen were supplied from the gas cylinders equipped with micrometric valves. Both reagents were passed through the columns with the molecular sieves 5A in order to remove the moisture. The flow rates of gases were measured using flow meters. The mixing of reagents was performed in a mixer. The reagents were passed by valve to the quartz reactor of an inside diameter 11 mm. The catalyst bed was placed on the grate from quartz wool. A resistance furnace heated the reactor. The measurement and control of temperature was ensured by the system: a thermocouple Fe—CuNi and temperature regulator with a digital meter. A receiver was used for the collection of the liquid fraction. The gas products were sampled through the membrane. Oxygen that comprised 15.5 % of the reaction mixture volume was used as an oxidant.

Contact time of the reaction mixture with the catalyst varied between 0.5 s and 2.5 s (1440—7200 h^{-1} space velocity at NTP) at a temperature ranging from 350 to 590 °C.

Kinetic studies were carried out in an integral-type reactor. Two series of measurements were conducted. During the first one the temperature was kept constant while the contact time was changed. In the other one, the process was carried out at different temperatures, with the same contact time.

The composition of products mixture was determined chromatographically. From the values of the mole fractions of the gases the values of partial pressure of the compounds were calculated.
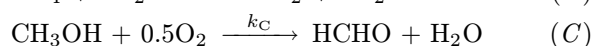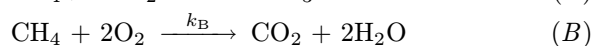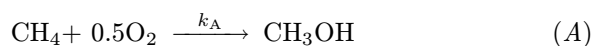
RESULTS AND DISCUSSION

In Figs. 1 and 2 variation of selectivity of the methane oxidation to methanol, formaldehyde, and carbon dioxide with the contact time is shown for the lowest and the highest reaction temperature. Prolonging the contact time for all catalysts at both temperatures resulted in the increase of carbon dioxide content in the post-reaction mixture. The higher the reaction temperature, the more vigorous increase of CO_2 yield was noted. For the Fe-NaZSM-5 catalysts, the carbon dioxide yield was lower than that of methanol when the reaction was carried out at low temperatures and for short contact time. Raising the temperature and Fe content resulted in the increase of methanol and carbon dioxide yield. Elongating the contact time

at low temperature resulted in higher methanol yield. At high temperature the lower CH_3OH yield was observed when the contact time was longer (Fig. 3).

The same phenomenon was observed with regard to Fe-HZSM-5. However, in this case carbon dioxide always turned out to be the principal reaction product, regardless of experimental conditions. Extending the contact time caused a very slow increase of the formaldehyde content in the products. On the other hand, a slight decline of the HCHO yield was observed when the Fe-NaZSM-5 catalysts were employed at higher temperatures.

Based on a thorough analysis of composition of the post-reaction mixture obtained under various reaction conditions, a set of reactions occurring in the reactor was assumed

$$CH_4 + 0.5O_2 \xrightarrow{\ k_A\ } CH_3OH \qquad (A)$$

$$CH_4 + 2O_2 \xrightarrow{\ k_B\ } CO_2 + 2H_2O \qquad (B)$$

$$CH_3OH + 0.5O_2 \xrightarrow{\ k_C\ } HCHO + H_2O \qquad (C)$$

$$HCHO + O_2 \xrightarrow{\ k_D\ } CO_2 + H_2O \qquad (D)$$

Then, the following reaction rate expressions have been suggested

$$r_{CH_3OH} = k_A \left(p_{CH_4}\right)^{N\left(A_{CH_4}\right)} \left(p_{O_2}\right)^{N\left(A_{O_2}\right)} - $$
$$- k_C \left(p_{CH_3OH}\right)^{N\left(C_{CH_3OH}\right)} \left(p_{O_2}\right)^{N\left(C_{O_2}\right)} \quad (1)$$

$$r_{CO_2} = k_B \left(p_{CH_4}\right)^{N\left(B_{CH_4}\right)} \left(p_{O_2}\right)^{N\left(B_{O_2}\right)} + $$
$$+ k_D \left(p_{HCHO}\right)^{N\left(D_{HCHO}\right)} \left(p_{O_2}\right)^{N\left(D_{O_2}\right)} \quad (2)$$

$$r_{HCHO} = k_C \left(p_{CH_3OH}\right)^{N\left(C_{CH_3OH}\right)} \left(p_{O_2}\right)^{N\left(C_{O_2}\right)} - $$
$$- k_D \left(p_{HCHO}\right)^{N\left(D_{HCHO}\right)} \left(p_{O_2}\right)^{N\left(D_{O_2}\right)} \quad (3)$$

r_x being the rate of generating the product x, k_A, k_B, k_C, k_D pressure reaction rate constants for the corresponding reactions (A—D), p_x partial pressure of the component x at the reactor outlet, and $N(I_x)$ order of reaction (1) related to the component x.

As a result of the numerical differentiation of the $p_x = f(\tau)$ equation, the instantaneous rate of generating the product for every contact time that was used during the measurements, was obtained. The reaction rate coefficient was determined with the help of the quasi-Newton method. It was concluded that satisfactory results were arrived at only when it was assumed that all the four reactions were of the zero order with respect to oxygen and of the first order with respect to the other substrate (methane, methanol, or formaldehyde). It is worth mentioning that *Spencer* and *Pereira* came up with a similar assumption while investigating the kinetics of methane partial oxidation with the molybdena-silica catalyst [3]. Hence, the kinetic equations were simplified giving the following forms
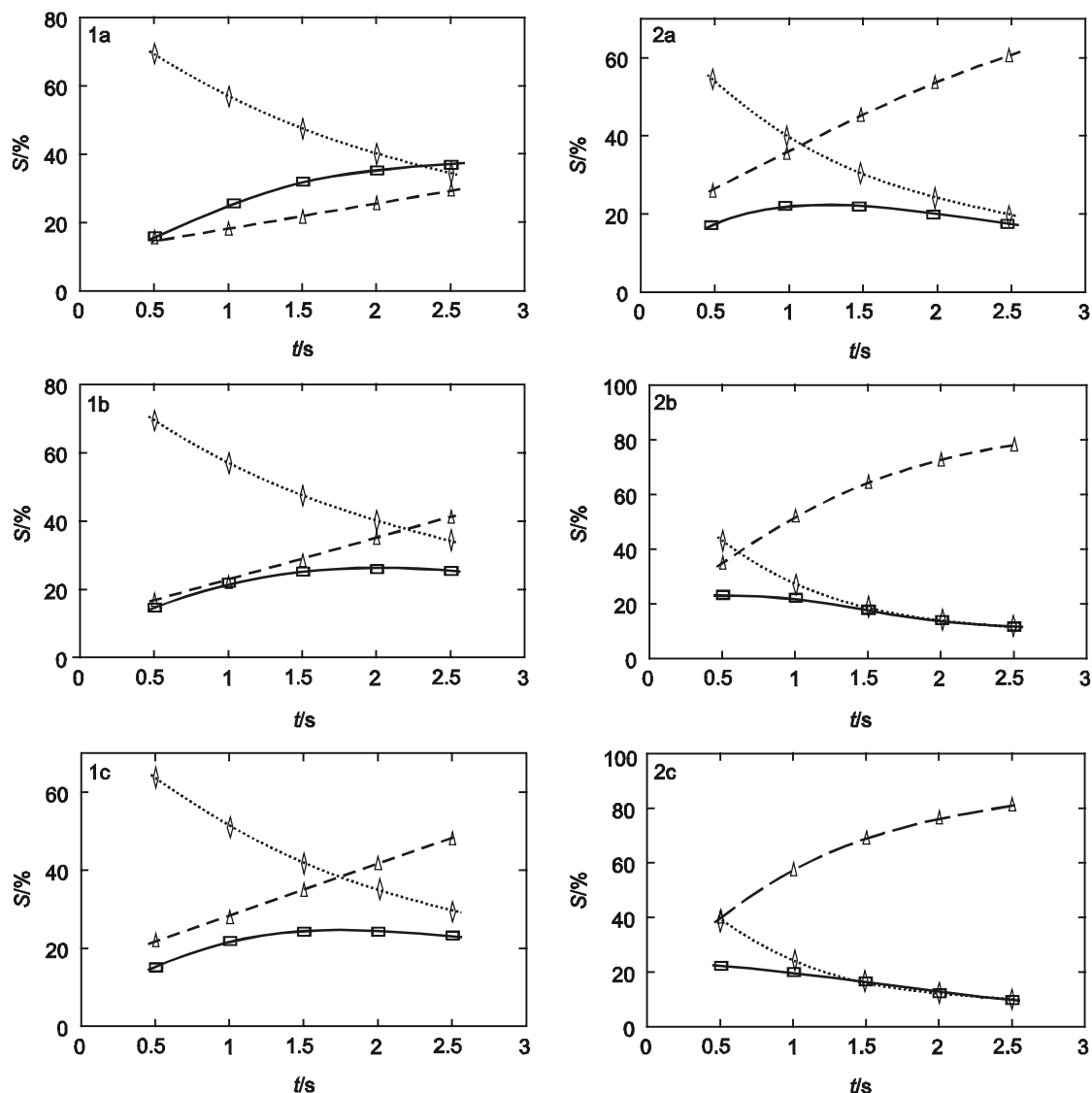
Fig. 1. The changes in the selectivity of methane oxidation to particular products with the extension of the contact time for the catalyst's hydrogen form. a – Fe-HZSM-5(45), b – Fe-HZSM-5(34), c – Fe-HZSM-5(22), 1 – temperature 350 °C, 2 – temperature 590 °C, diamond and dotted line – methanol, rectangle and straight line – formaldehyde, triangle and dashed line – carbon dioxide.

$$r_{CH_3OH} = k_A p_{CH_4} - k_C p_{CH_3OH} \qquad (4)$$
$$r_{CO_2} = k_B p_{CH_4} + k_D p_{HCHO} \qquad (5)$$
$$r_{HCHO} = k_C p_{CH_3OH} - k_D p_{HCHO} \qquad (6)$$

Fig. 4 presents Arrhenius plot of reaction rate constants for the six catalysts. Their rectilinear course confirms the accuracy of the previously assumed set of equations.

Analysis of the value of reaction rate coefficients obtained at different temperatures in the presence of various catalysts allowed formulating the following conclusions. The highest rate of methanol production, reaction (A), was observed when the Fe-HZSM-5(22) catalyst was used. The decline of the iron content in the catalysts results in the decrease of methane to methanol oxidation rate. Use of H-ZSM-5 instead of the corresponding sodium zeolite form having the

same atomic ratio n(Si) : n(Fe) resulted in an increase of the rate of methane oxidation to methanol.

The rate of methanol oxidation to formaldehyde, reaction (C), was significantly higher when the Fe-NaZSM-5 catalysts were used. Iron content in both forms of catalysts (Na and H) was directly proportional to the observed rate of methanol oxidation. When Fe-HZSM-5(45) was used as catalyst, the unwelcome process of methanol oxidation was performed the most slowly.

The dependence between the iron content, the catalyst form (Na or H), and the rate of formaldehyde oxidation, reaction (D), was similar to that of the reaction (C).

Direct methane oxidation to carbon dioxide, reaction (B), was the most intense in the presence of Fe-HZSM-5(22) catalyst. The decline of the iron content
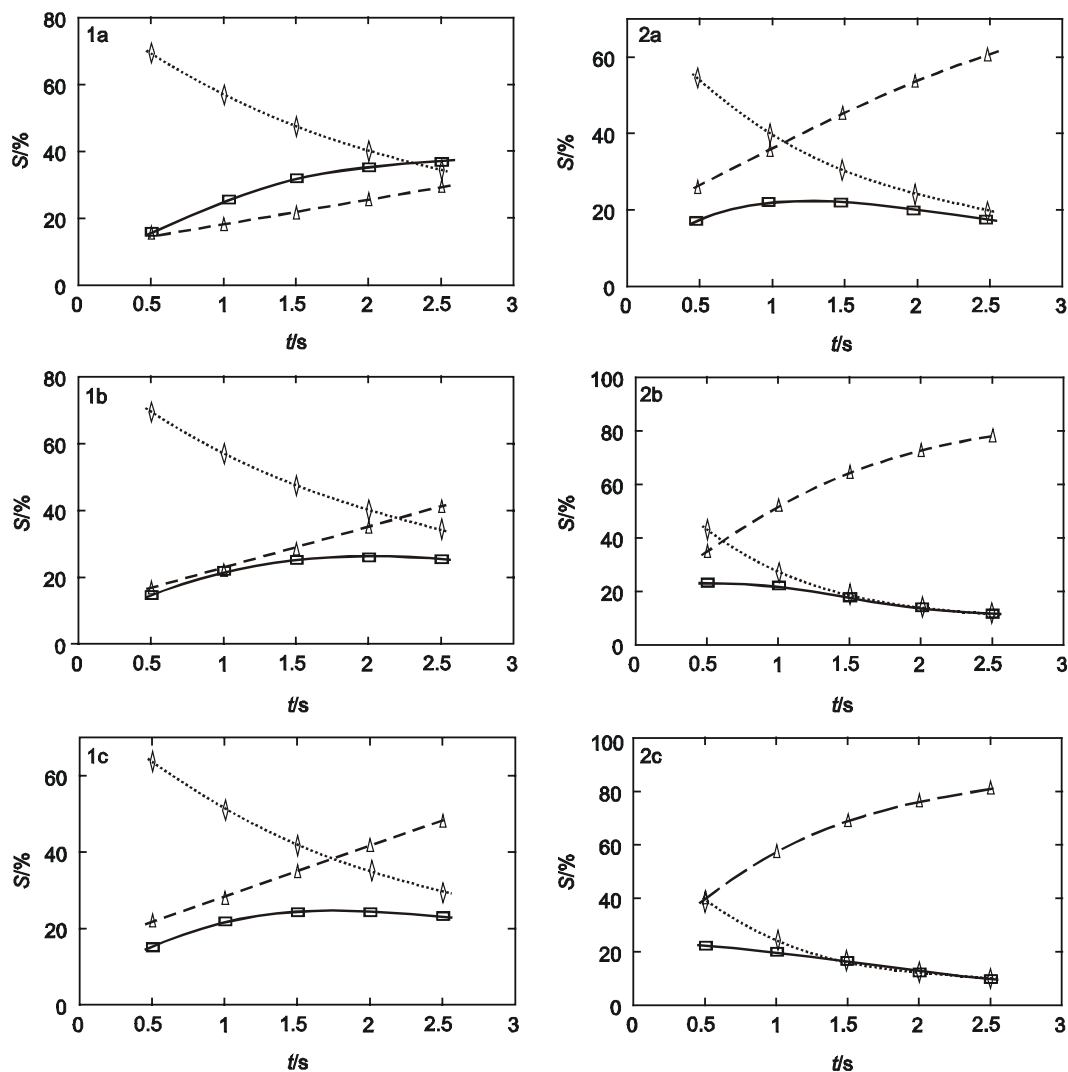
Fig. 2. The changes in the selectivity of methane oxidation to particular products with the extension of the contact time for the catalyst's sodium form. a – Fe-NaZSM-5(45), b – Fe-NaZSM-5(34), c – Fe-NaZSM-5(22), 1 – temperature 350 °C, 2 – temperature 590 °C, diamond and dotted line – methanol, rectangle and straight line – formaldehyde, triangle and dashed line – carbon dioxide.
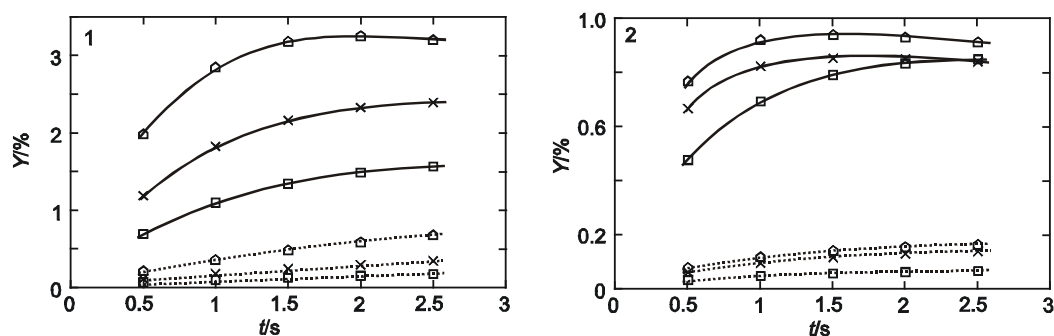

Fig. 3. The changes in the methanol yield with the extension of the contact time. 1 – H form, 2 – Na form, dotted line – 350 °C, straight line – 590 °C, rectangle – Si : Fe = 45, cross – Si : Fe = 34, house – Si : Fe = 22.

caused the decrease of the reaction (B) rate. It is clear that this reaction was much faster in the presence of H-ZSM-5-based catalysts.

The pressure rate coefficients, k_i, were recalcula-
ted to give concentration rate coefficients, k_{ci}, in order to determine the activation energy for reactions (A—D). Next, the activation energy for reactions (A—D) was calculated on the basis of the inclination angle
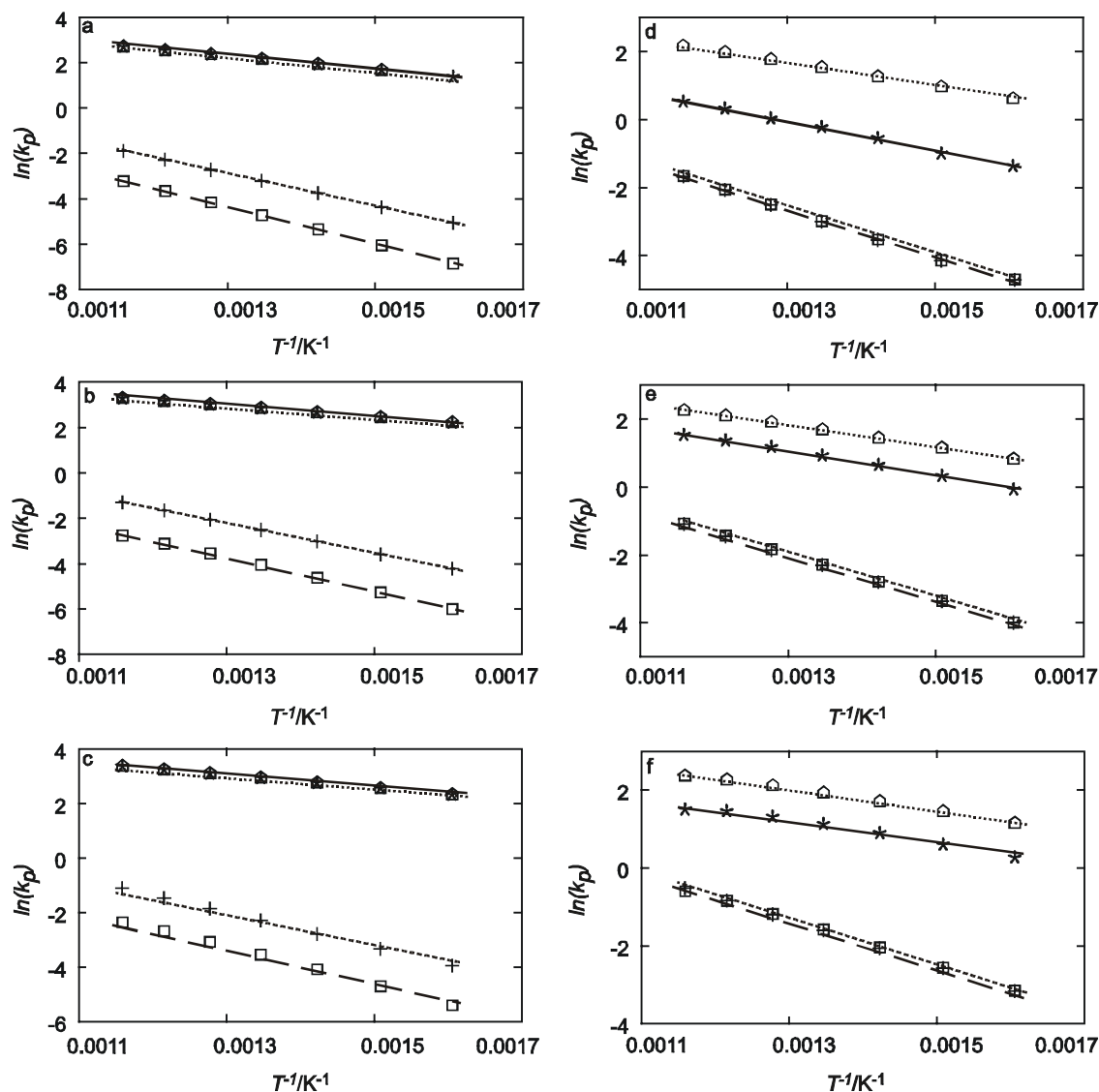
Fig. 4. Arrhenius plot of the reaction rate constants k_A (plus and short dashed line), k_B (square and long dashed line), k_C (house and dotted line), and k_D (asterisk and straight line) for the catalysts: a – Fe-NaZSM-5(45), b – Fe-NaZSM-5(34), c – Fe-NaZSM-5(22), d – Fe-HZSM-5(45), e – Fe-HZSM-5(34), and f – Fe-HZSM-5(22).

of the straight line: $\ln(k_{ci}) = \ln(A) - E/RT$. Table 1 summarizes the values of apparent activation energy, E, of all reactions in the presence of all catalysts investigated. Increase of the iron content in the catalyst leads to the decline of the values of apparent activation energy. The value of activation energy depends on the number of active species generated by iron. Different forms of iron have been identified in Fe-ZSM-5 [17]: isolated ions either in framework positions or in cationic positions in the zeolite channels, binuclear and oligonuclear iron complexes in extraframework positions, iron oxide FeO_x nanoparticles and large iron oxide particles (Fe_2O_3). It is difficult to distinguish which one is important for the reactions $(A\!-\!D)$. It is evident that the activation energy values E_A and E_B for the same catalyst were similar. Both forms (Na and H) of the catalyst having the

same iron content revealed insignificant differences between the corresponding values of apparent activation energy. The activation of methane (reactions (A) and (B)) took place on the same catalytically active centres.

The values of activation energies for the oxidation of methanol and formaldehyde were significantly lower than the values of E_A and E_B. The activation of methane and oxygenates (CH_3OH and $HCHO$) needed different active species. Markedly lower values of E_C and E_D were observed when sodium form of the catalyst was used compared to the corresponding Fe-HZSM-5 one. Because of acid properties of methanol and formaldehyde these compounds could be more easily oxidized on Na than on H forms of ZSM-5.

The highest methanol and formaldehyde yield was 3.16 % and 4.52 %, respectively. These values were

Table 1. Apparent Activation Energy of Reactions (A—D) in the Presence of Investigated Catalysts

Si : Fe atomic ratio		Apparent activation energy, E_i/(kJ mol^{-1})			
		(A)	(B)	(C)	(D)
H-ZSM-5	45	64776	65042	35873	41834
	34	60237	60305	34534	35972
	22	55416	54241	31933	29839
Na-ZSM-5	45	65026	73680	31178	30719
	34	60610	66995	26553	26198
	22	59150	63247	25823	25395

achieved over Fe-HZSM-5 at 590 °C and after 2.5 s contact time.

SYMBOLS

A	frequency factor	
k	pressure rate coefficient	mol dm^{-3} s^{-1} MPa^{-1}
k_c	concentration rate coefficient	s^{-1}
E	activation energy	J mol^{-1}
T	temperature	K
t	time	s
r	reaction rate	mol dm^{-3} s^{-1}
p	component partial pressure	MPa
S	product selectivity	mol %
R	universal gas constant	kJ mol^{-1} K^{-1}

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