

High-temperature methane oxidation over metallic monolith-supported zeolite catalysts containing Mn, Co, and Pd ions

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The high-temperature complete oxidation of methane over metallic monolith-supported zeolite catalysts containing isolated Mn, Co, and Pd ions was studied. The reaction involves heterogeneous and heterogeneous-homogeneous catalytic processes. The ratio between these processes depends on the temperature, feed rate, and the amount of catalyst charged in the reactor. In the heterogeneous catalytic process, the activity of the catalysts supported on the Fe–Cr–Al monolithic alloy decreases in the series Pd > Mn > Co > Fe–Cr–Al monolith and the reaction rate uniformly increases with increasing contact time. In the heterogeneous-homogeneous process, the reaction rate drastically increases and a 100% conversion of methane to CO₂ can be achieved by minor variations of the contact time. In this case, methane oxidation depends not only on the catalyst chemical composition but also on its external surface area and the reaction volume.

Key words: methane, oxidation, monolith catalyst, zeolite, palladium, manganese, cobalt.

A search of catalysts for the high-temperature hydrocarbon oxidation is an important problem despite the numerous works that have been reported in the past decade.^{1–8}

The thermally stable (up to 1000 °C) high-silica ZSM-5 zeolites containing isolated transition metal ions are promising systems for high-temperature methane oxidation. We have found previously a good performance of these systems in the high-temperature complete oxidation of methane.^{9–12}

This work is aimed at studying the high-temperature methane oxidation over the metallic monoliths-supported ZSM-5 zeolites containing isolated Pd, Mn, and Co ions. It was of interest to find conditions favorable for the heterogeneous catalytic and heterogeneous-homogeneous processes and to study sensitivity of these processes to the catalyst chemical composition.

Experimental

High-silica zeolite TsVM (Si/Al = 20), structural analog of ZSM-5 (Nizhegorodskii Sorbent Co Ltd), was used for the preparation of Mn- and Co-containing zeolite catalysts, and ZSM-5 (PQ Corporation, Si/Al = 25) was used for the preparation of the Pd-containing catalyst. To introduce a metal, the starting ammonium zeolite was impregnated to incipient wetness with an aqueous solutions of Mn(NO₃)₂, Co(NO₃)₂, and Pd amino-nitrile complex. The samples prepared were dried in air for 6 h at 20 °C and 4 h at 140 °C followed by calcination in an air flow for

2 h at 500 °C. The catalysts 3% Mn/ZSM-5, 2% Co/ZSM-5, and 1% Pd/ZSM-5 were prepared by this procedure. The content of the isolated metal ions in these samples corresponded to the maximal value achievable by the introduction of these metals in zeolite by a topochemical reaction.^{10–13}

To prepare the monolith catalysts, the metal-containing zeolites were supported on a foil of the thermally stable Fe–Cr–Al alloy with a thickness of 80 µm. The oxide layer was deposited by electrophoretic precipitation according to a known procedure.¹⁴ Aluminum hydroxide sol was used as binder. A starting suspension used for deposition contained a fine powder of ZSM-5 (8.2 g L⁻¹, particle size 5–10 µm) in an EtOH sol of aluminum hydroxide ($C_{Al(OH)} = 8.2 \text{ g L}^{-1}$), and the deposit thickness was ~10 µm. After precipitation, the samples were dried in air for 36 h at 20 °C and then heated for 2 h at 500 °C. The smooth and crimped foil layers covered on both sides with the zeolite were lumped together and rolled into a tube with a height of 2.6 cm and a cross-section area of 4.1 cm². The monoliths prepared had 40 triangle channels per 1 cm². The amount of the catalyst in the monoliths was 0.06–0.07 g. Such a deposition technique of the catalysts on the metallic monoliths allowed us to operate with small specimens of highly active catalysts at high feeding rates of the reaction mixture.

Complete methane oxidation was conducted in a flow setup at atmospheric pressure with the 10–1900 cm³ min⁻¹ feed rate of the initial gas mixture (2.5 vol.% CH₄ in air). To study the catalytic performance, the monoliths were placed on a grate positioned 4 cm above the bottom of the quartz reactor (Fig. 1). Nichrome wire of a heater was uniformly wound over the whole length of the reactor and covered by a glass jacket only to provide fast heat exchange with environment. The temperature was controlled and measured with a TPM-10 thermal controller

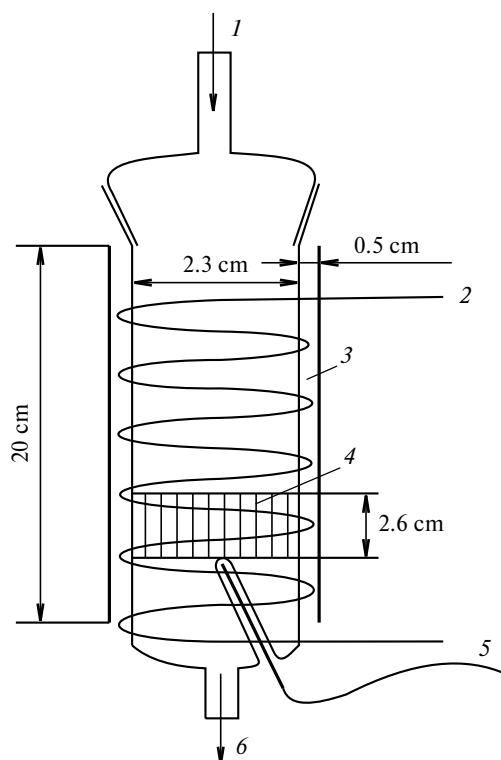


Fig. 1. Scheme of the reactor for high-temperature methane oxidation to CO_2 : 1, inlet of the reaction mixture; 2, spiral of the heater; 3, glass jacket; 4, monolith catalyst; 5, thermocouple; 6, outlet of the reaction products to analyzer.

with an accuracy of $\pm 0.1\%$. The temperature gradient over the reactor height measured at 500 and 700 $^{\circ}\text{C}$ was $1\text{ }^{\circ}\text{C cm}^{-1}$. The runs were performed in an air flow, which was fed with the reaction mixture to a top of the reactor. A thermocouple for temperature controlling was placed in the center of the reactor. The feed rate for air was the same as that for the reaction mixture, thus eliminating a possible high temperature gradient, which could be created by the heater. The isothermicity in the catalyst layer during oxidation was verified by the kinetic method¹⁵, according to which the specific reaction rates should remain constant when the catalyst charge changes at a specified temperature. The specific activity (reaction rate) of the 3% Mn/ZSM-5 monolith catalyst was found to remain constant upon doubling the catalyst bed depth of the reactor. When the charge of the catalyst was increased by 2, 3, and 4 times, its specific activity remained constant.¹⁶ This indicates that the heterogeneous catalytic methane oxidation occurs under the isothermal conditions in the kinetic region over the whole catalyst volume.^{15–17}

The desired temperature of methane oxidation, which was continuously measured with a temperature controller, remained constant during all the runs. A temperature increase due to the heat evolution during oxidation was monitored with a thermocouple located under the grate with the catalyst. When the temperature increased, the thermocouple response was transmitted to the thermal controller, which turned off the heater. Fast heat exchange with environment resulted in establishing a desired temperature, so that the isothermal conditions were maintained in the reaction volume.

When the contact time (τ) was varied, an increase and decrease in the amount of CO_2 formed were reversible.

Methane oxidation over the Mn/ZSM-5 catalyst was studied on both one and two monoliths positioned one above another. Methane oxidation over the other catalysts was studied with one monolith. During the run, the temperature of the reaction mixture flow was increased from 500 to 720 $^{\circ}\text{C}$ and then decreased to 600 or 500 $^{\circ}\text{C}$, and new runs were performed to verify the reproducibility of results and the thermal stability of the catalyst. The activities of the cobalt and palladium catalysts were also studied after their heat treatment in the reaction mixture at 800 and 900 $^{\circ}\text{C}$. Conversions (α) of CH_4 to CO_2 found by enhancing contact times coincided completely with those measured upon the subsequent decrease in τ .

The reaction products were analyzed by GC on a column packed with Polysorb-1 (heat conductivity detector, helium carrier gas, temperature 25 $^{\circ}\text{C}$).

Earlier,^{10–13} in studies of methane oxidation over the catalysts used in this work, we measured the amounts of CH_4 reacted and those of CO_2 formed, and no reaction products besides CO_2 and H_2O were found. Therefore, in this work the amount of CO_2 formed was used as the measure of methane conversion. In some runs, the amount of CO_2 was 2.5 ± 0.02 vol.% and this corresponded to complete oxidation of 2.50 vol.% CH_4 contained in the initial mixture.

The activation energy of reaction was calculated from the temperature dependence of the feed rates of the initial mixture (v), which correspond to the specified conversion α , or $v \cdot \alpha$ values when the kinetics was described by the zero-order equation.¹⁸ The contact time for the monolith zeolite catalysts was calculated as the ratio between the monolith volume and the feed rate of the initial mixture. The feed rate of the initial mixture at the specified conversion was taken as the catalyst activity (A).¹⁹ Calculations were carried out by the equation $A = v\alpha C / 22.4 m_M$, where C is the methane concentration in the initial mixture and m_M is the content of the transition metal in the catalyst.

Results and Discussion

We studied the activity of the monolith zeolite catalysts in a high-temperature region (500–900 $^{\circ}\text{C}$). Under these conditions the mass-transfer processes and homogeneous-heterogeneous chain reactions can affect the heterogeneous catalytic methane oxidation. To determine whether the heterogeneous catalytic or homogeneous-heterogeneous chain reactions occur, we used the specific kinetic features^{20–22} typical of these processes.

The main features of the heterogeneous catalytic process are as follows: (1) specific activity is independent of the catalyst charge and the volume of the reaction space; (2) drastic changes in the reaction rate when varying the contact time are absent; (3) activation energy for methane oxidation is lower than that for the homogeneous-heterogeneous process.

The main features of the homogeneous-heterogeneous chain process are as follows: (1) specific activity changes when the catalyst charge or the reaction space volume is

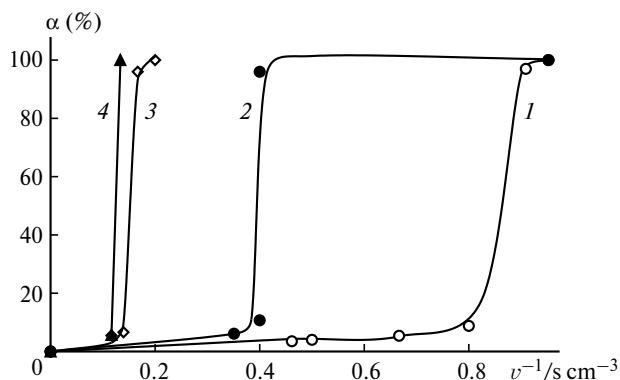


Fig. 2. Methane conversion to CO_2 (α) vs. reverse gas feed rate (v^{-1}) in the empty reactor at 650 (1), 670 (2), 700 (3), and 720 °C (4).

varied; (2) reaction rate increases dramatically when the contact time increases slightly; (3) activation energy for methane oxidation is higher than that for the heterogeneous catalytic process but lower than that for the homogeneous reaction.

Methane oxidation in empty reactor. No methane oxidation to CO_2 in the empty reactor was found at temperatures below 650 °C. An induction period was observed at 650 °C, and during this period the CH_4 conversion increases slightly from 5 to 9% with decreasing feed rate of the initial mixture but then increases sharply to 97–100% (Fig. 2). Such a sharp increase in the reaction rate is typical of radical-chain processes. At higher temperatures, the methane oxidation rate sharply increases at higher feed rates of the initial mixture and the CH_4 conversion is at most 6–10% during the induction period. The activation energy for methane oxidation in the empty reactor calculated from the temperature dependence of the feed rate of the initial mixture at $\alpha \approx 100\%$ is $200 \pm 15 \text{ kJ mol}^{-1}$.

Methane oxidation over metallic monolith. Methane oxidation over the metallic monolith begins at 600 °C, *i.e.*, under the conditions when the reaction in the empty reactor does not occur (Fig. 3). The CH_4 to CO_2 conversion smoothly increases to 20% with increasing contact time as shown by the initial segment of the kinetic curve. Then the reaction rate drastically increases and the conversion achieves 80–100%. The activation energy of methane oxidation calculated from the temperature dependence of the feed rate of the initial mixture is the same at $\alpha = 15\%$ and $\alpha \approx 100\%$ and is equal to $160 \pm 10 \text{ kJ mol}^{-1}$. The contact time, which corresponds to a sharp increase of the methane conversion, decreases from 7 to 0.6 s with increase in the temperature from 600 to 650 °C.

Methane oxidation over catalyst 3% Mn/ZSM-5. Complete oxidation of CH_4 to CO_2 over the catalyst 3% Mn/ZSM-5 supported on the metallic monoliths was studied in the temperature range of 500–720 °C at the contact times of 0.5–35 s and conversions of 8–99%.

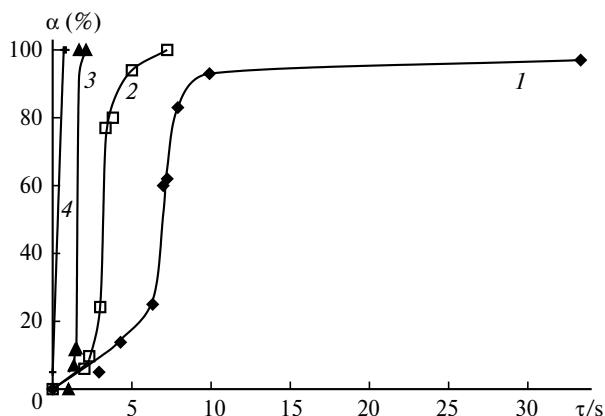


Fig. 3. Methane conversion to CO_2 (α) vs. contact time (τ) over the metallic monolith without oxide coverage at 600 (1), 620 (2), 680 (3), and 700 °C (4).

The catalyst 3% Mn/ZSM-5 is thermally stable in the temperature range studied. As can be seen in Fig. 4, *a*, the methane conversion at 500 °C increases steadily with increasing contact time and is independent of the catalyst charge in the reactor (*viz.*, one or two monoliths) at the same contact times. In the runs with two monoliths at

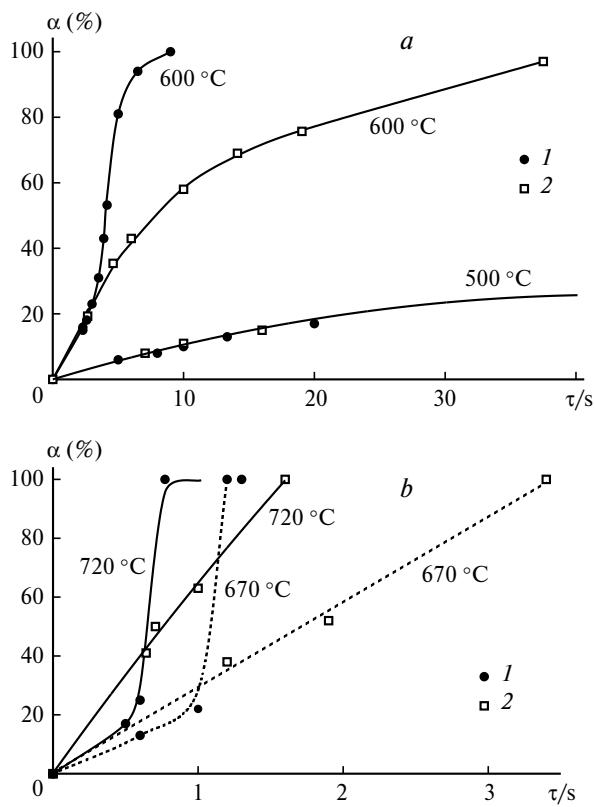


Fig. 4. Methane conversion to CO_2 (α) vs. contact time (τ) over the metallic monolith catalyst containing 3% Mn/ZSM-5 at 500 and 600 °C (a), 670 and 720 °C (b). The runs were performed over one (1) and two monoliths (2).

600, 670, and 720 °C, the methane conversion monotonously increases with contact times without sharp jumps as was observed in the runs at 500 °C. The conversion at 670 and 720 °C in the range from 8 to 99% (Fig. 4, *b*) increases proportionally to the contact time, indicating the zero order of the reaction. The same reaction order was found at 500 and 600 °C but at the conversion below 20%. The activation energy for methane conversion to CO₂ is 130±10 kJ mol⁻¹. The same activation energy has been found for the pelleted sample.¹⁰ This coincidence indicates that the nature of CH₄ to CO₂ oxidation over the 3% Mn/ZSM-5 catalyst remains unchanged when the reaction was conducted over the catalyst supported on the metallic monolith and the reaction temperature was increased to 720 °C.

Thus, the specific activity of the catalyst 3% Mn/ZSM-5 in the form of two monoliths is independent of its amount; sharp changes in the reaction rate with a slight variation of the contact time (by 10–15%) are not found, and the activation energy is substantially lower than those of the homogeneous process in the empty reactor and homogeneous-heterogeneous process over the metallic monolith. On the basis of the above kinetic features one can conclude that methane oxidation over two monoliths of the 3% Mn/ZSM-5 catalyst is the heterogeneous catalytic process.

The external-diffusion retardation does not affect the heterogeneous catalytic complete oxidation of CH₄ up to 720 °C and $\alpha \approx 99\%$, and this is confirmed by the absence of sharp kinks on the logarithmic dependence of $\alpha \cdot v$ on $1/T$ (Fig. 5) and the fact that the plots of methane conversion vs. contact time for two different catalyst layers in the reactor at two temperatures of 500 and 600 °C coincide (see Fig. 4, *a*).

When the catalyst charge is halved (*viz.*, one of monoliths is removed), methane oxidation changes drastically. Beginning from 600 °C, one can distinguish two sections

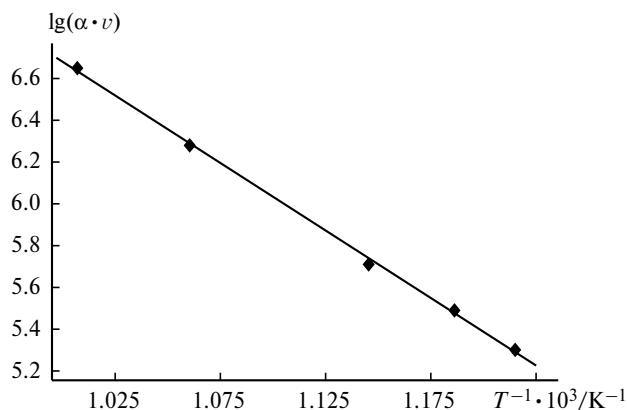


Fig. 5. Activity of the metallic monolith catalyst containing 3% Mn/ZSM-5 vs. inverse temperature in complete methane oxidation (α is conversion, v is the feed rate of the initial mixture).

on the plot of α vs. τ (see Fig. 4, *a*, *b*). As indicated by the first section ($\alpha < 20$ –30%), the methane conversion nearly coincides with that over two monoliths, *i.e.*, the reaction is a heterogeneously catalyzed process. At $\alpha > 20$ –30%, a slight increase in the contact time (by 10–15%) results in a sharp increase in the reaction rate and in methane conversion to CO₂ up to 94–100%. The desired temperature remains constant during the whole run. The contact time at which the above transition occurs decreases from 3 to 0.6 s as temperature increases from 600 to 700 °C. The activation energy calculated from the temperature dependence of the feed rate of the initial mixture at $\alpha \approx 100\%$ is 155±5 kJ mol⁻¹. This value is higher than the activation energy of the heterogeneous process (130 kJ mol⁻¹) and that of methane oxidation in the empty reactor (200 kJ mol⁻¹).

Thus, during methane oxidation to CO₂ over one monolith, one can observe that at the temperatures 600–720 °C and $\alpha > 20$ –30% under isothermal conditions, the amount of CO₂ increases markedly with a low (10–15%) variation of the contact time. In addition, with increasing catalyst amount in the reaction volume there is a decrease in the reaction rate. Finally, the activation energy enhances compared to those typical of the heterogeneous catalytic regime. The kinetic features of the reaction allow suggestion that methane oxidation to CO₂ over one monolith at 600–720 °C and $\alpha > 20$ –30% is the heterogeneous-homogeneous chain process.

Since in the experiments with one monolith one can simultaneously study methane oxidation in both heterogeneous catalytic and heterogeneous-homogeneous processes, the performance of the palladium and cobalt catalysts was studied under these conditions.

Methane oxidation over catalyst 1% Pd/ZSM-5. Complete methane oxidation to CO₂ over the catalyst 1% Pd/ZSM-5 supported on a metallic monolith was studied at the temperatures of 500–720 °C and conversions of 10–100% (Fig. 6, *a*, *b*). In this temperature range at the conversions up to 40–50%, the methane conversion gradually increases with increasing contact time. The activation energy calculated at $\alpha = 30\%$ is 84±5 kJ mol⁻¹. The reaction rate sharply increases with further increasing the contact time and the conversion reaches 97–100%. When the reaction temperature is increased from 550 to 720 °C, the contact time relevant to this increase decreases from 3 to 0.5 s. The activation energy calculated at conversions close to 100% is 156±5 kJ mol⁻¹. Thus, for methane oxidation over the palladium catalyst as well as over the Mn-containing catalyst, one can distinguish two regions, which differ essentially in the kinetic features and activation energies. One can assume that in these regions, two different mechanisms, the heterogeneous catalytic and chain heterogeneous-homogeneous mechanisms, are operative in the reaction.

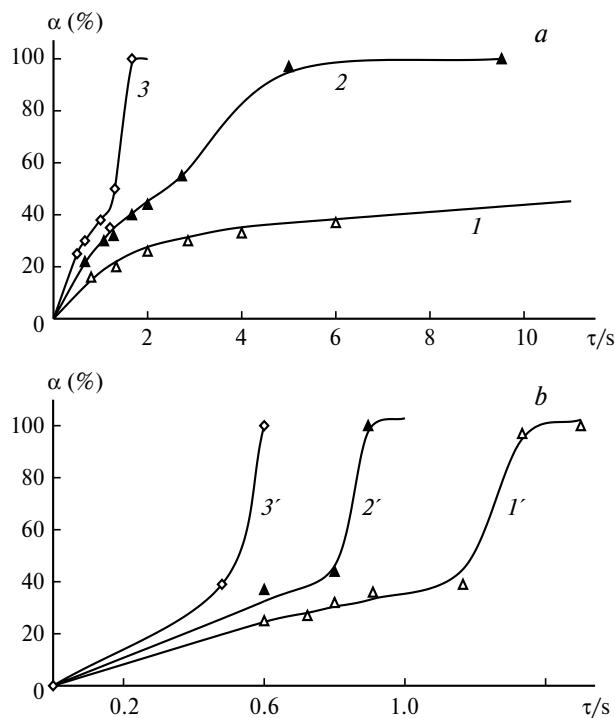


Fig. 6. Methane conversion to CO_2 (α) vs. contact time (τ) over the metallic monolith catalyst containing 1% Pd/ZSM-5 at 500 (1), 550 (2), 600 °C (3) (a) and 650 (2'), 700 (1'), 720 °C (3') (b).

Methane oxidation over catalyst 2% Co/ZSM-5. On inspecting the plot of methane to CO_2 conversion vs. contact time obtained for the catalyst 2% Co/ZSM-5 supported on the metallic monolith (Fig. 7), one can also find two sections. At $\alpha < 25\%$, the conversion is proportional to the contact time, and this is typical of a zero-order heterogeneous reaction. The activation energy calculated at $\alpha = 20\%$ and temperatures of 550–700 °C is $198 \pm 10 \text{ kJ mol}^{-1}$. This value coincides with the activation

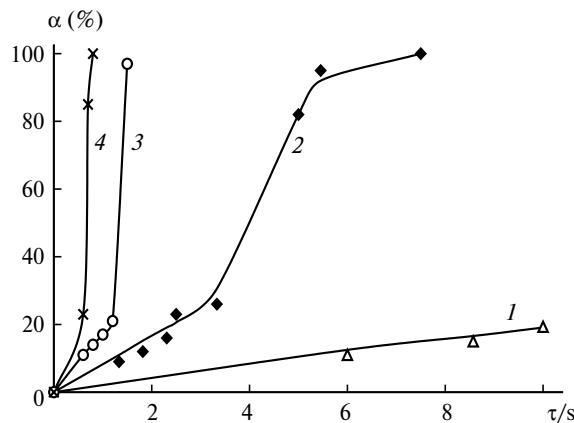


Fig. 7. Methane conversion to CO_2 (α) vs. contact time (τ) over the metallic monolith catalyst containing 2% Co/ZSM-5 at 550 (1), 600 (2), 650 (3), and 700 °C (4).

energy over the pelleted catalyst 2% Co/ZSM-5, which was calculated for heterogeneous catalytic oxidation of CH_4 at 450–500 °C in the kinetic regime.¹²

The second section of the plot of methane conversions vs. contact time (see Fig. 7) shows that the methane conversion to CO_2 under isothermal conditions sharply increases at $\alpha > 20\%$ achieving 95–100%. The increase in α is likely due to the transition from the heterogeneous catalytic process to the chain heterogeneous-homogeneous process. The contact time at which this transition occurs decreases from 3.5 to 0.5 s with an increase in temperature from 600 to 700 °C. The activation energy of the heterogeneous-homogeneous process is 165 kJ mol^{-1} as in the case of the manganese and palladium catalysts.

Hence, two pathways of methane oxidation to CO_2 occur over the Pd-, Mn-, and Co-catalysts as well as over the metallic monolith without an oxide layer: one is a heterogeneously catalyzed reaction and another is a chain heterogeneous-homogeneous reaction. Their ratio changes with the feed rate of the initial mixture, reaction temperature, and a depth of the catalyst bed (charge). Only heterogeneous-homogeneous methane oxidation occurs in the empty reactor. The above findings allow some general conclusions to be drawn on the kinetic features of high-temperature methane oxidation.

The heterogeneous catalytic process prevails at low contact times and CH_4 conversions below 50%. The catalytic activity decreases in the series Pd/ZSM-5 > Mn/ZSM-5 > Co/ZSM-5 > Fe–Cr–Al-monolith (Fig. 8, a, Table 1). The activation energy for methane

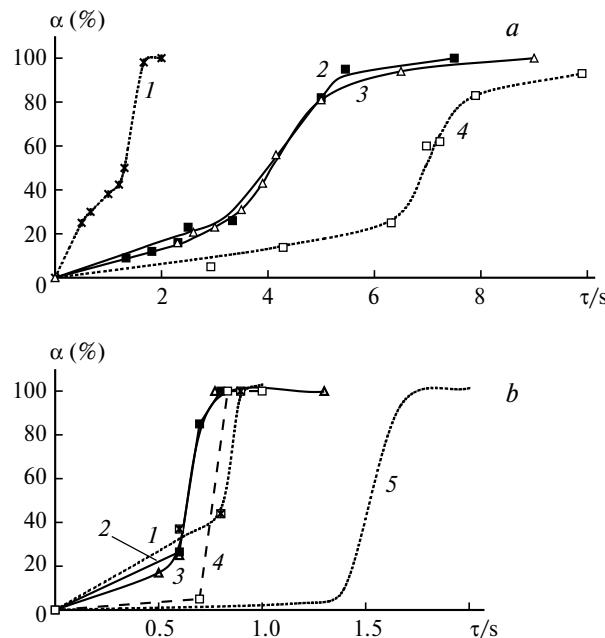


Fig. 8. Methane conversion to CO_2 (α) vs. contact time (τ) at 600 (a) and 700 °C (b) over the catalysts 1% Pd/ZSM-5 (1), 2% Co/ZSM-5 (2), 3% Mn/ZSM-5 (3), Fe–Cr–Al-monolith (4) and in the empty reactor (5).

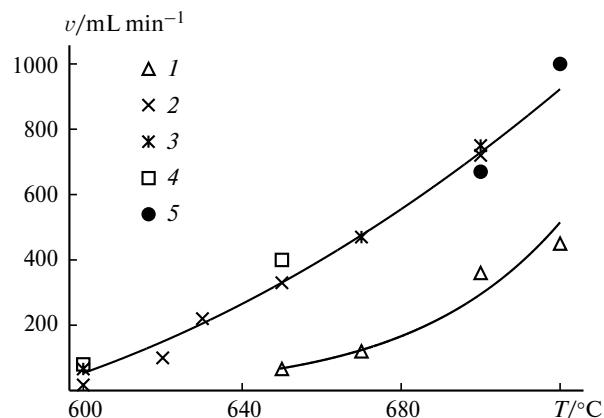
Table 1. Catalytic activity (A) and activation energy (E) for complete methane oxidation at 500 °C and 33% conversion

Catalyst	A /mol (g metal h) $^{-1}$	E /kJ mol $^{-1}$
1% Pd/ZSM-5	4.4	84
3% Mn/ZSM-5	0.12	130
2% Co/ZSM-5	0.029	193
Fe—Cr—Al-monolith	—	160
10% Pd/Al ₂ O ₃ ^a	0.35	—
0.3% Pt/Al ₂ O ₃ /Ni ^b	0.17	—
CeO ₂ , barium hexaaluminat ^c	0.01	—

^a See Ref. 23.^b See Ref. 24.^c See Ref. 7.

oxidation over these catalysts increases in the same sequence. The zeolite catalysts studied in this work exceed in the specific activity measured at 500 °C the oxide Ba—Al-catalyst for methane combustion in gas turbines.^{1–8} In addition, the activity of the Pd-zeolite catalyst is many times higher than those of aluminum-palladium and aluminum-platinum catalysts (see Table 1). The high activity of metal-containing zeolite catalysts is due to the presence of metals in the zeolite lattice in the form of isolated ions.

The heterogeneous-homogeneous chain process of methane oxidation occurs at higher contact times and is accompanied by a sharp increase in the CO₂ amount induced by small changes of the feed rate of the gas mixture. The heterogeneous-homogeneous chain process begins at 550 °C over the most active catalyst and at 600 °C over all the rest catalysts, *i.e.*, by 50 °C lower than in the empty reactor. As can be seen in Fig. 8, *a*, chemical composition of the catalysts affects the rate of the heterogeneous-homogeneous process at 600 °C. Transition from the heterogeneous catalytic to significantly faster heterogeneous-homogeneous chain process occurs at different contact times over various catalysts. These differences (Fig. 8, *b*) vanish upon the further increase in temperature. As can be seen in Fig. 9, the CH₄ conversions to CO₂ close to 100% are achieved at nearly the same volume feed rates for the gas mixture (contact times) over all the catalysts including the metallic monolith. The activation energies of the heterogeneous-homogeneous process unlike those of the heterogeneous catalytic processes are also the same for all the catalysts and equal to 160±5 kJ mol $^{-1}$. Hence, chemical composition of the catalysts studied, while strongly affecting the catalyst activity in methane oxidation *via* the heterogeneous catalytic mechanism, does not essentially influence methane oxidation through the heterogeneous-homogeneous chain mechanism. The metallic monolith without the oxide coverage does not differ in

**Fig. 9.** Activity (feed rate of the reaction mixture (v) at ~100% methane conversion) vs. reaction temperature over various zeolite metallic monolith catalysts: 1, empty reactor; 2, metallic monolith; 3, Mn/ZSM-5; 4, Co/ZSM-5; 5, Pd/ZSM-5 (650 °C).

activity from the monolith with the supported Pd-zeolite catalyst.

When the catalyst amount is doubled (*viz.*, two instead of one monoliths are used), a decrease rather than an increase in the reaction rate was observed down to the value, which is immeasurable under the experimental conditions. The structural characteristics of the system (*viz.*, the external surface area (S) and reaction volume (V_r)), which would be capable of markedly affecting the rate of methane oxidation through the heterogeneous-homogeneous chain mechanism,^{20–22,25–28} are the same for all the catalysts and metallic monolith under study. The ratio S/V_r is constant in the runs with both one and two monoliths. When the heterogeneous-homogeneous process occurs in the absence of the catalyst and when the S/V_r ratio changes markedly, the methane conversions decrease more than 2 times (see Fig. 8) and the activation energy increases from 165 to 200 kJ mol $^{-1}$.

Hence, the catalytic high-temperature methane oxidation can occur both through heterogeneous catalytic mechanism and through the heterogeneous-homogeneous chain mechanism. In the first case, chemical composition of the catalyst is a determining factor for the methane conversion, while in the second case, the S/V_r ratio is one of the decisive factors. It follows that one should be careful in prediction of the catalytic activity at high temperatures on the basis of the data obtained under the conditions of the heterogeneous catalytic mechanism only.

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