Time-on stream behavior of Pd-, Co-, and Mn-zeolite catalysts supported on metal blocks in high-temperature methane oxidation

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Stability of the Pd-, Co-, and Mn-zeolite catalysts supported on metal blocks was studied in high-temperature methane oxidation. The temperature regions were found in which the starting catalysts exhibit stable performance. The temperature was determined at which a partial deactivation is followed by stabilization of catalysts in reaction environment. In terms of specific activity, the partially deactivated Pd-zeolite catalyst is several times more active than conventional oxidation catalysts Pd/Al_2O_3, Pt/Al_2O_3, and the most active oxide $CeO \cdot 6Al_2O_3$.

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

Stable performance of catalysts plays an important role in high-temperature methane oxidation.[1—8] The catalysts with a developed surface and high activity must operate for a long time in a humid reaction environment without losing these properties.

The most active catalysts Pd/Al_2O_3 and Pt/Al_2O_3 exhibit a low stability, and their activities decrease continuously with the time-on stream at $T > 600$ °C. The reasons for deactivation can be both a significant decrease in the surface of the active component because of sintering and the reduction of Pd and Pt ions. Attempts to improve the time-on stream behavior through the introduction of various additives to Al_2O_3 or the substitution of the latter by other supports with different chemical compositions produced no positive results. Perovskites and hexaaluminates are more stable but lower active than catalysts containing noble metals.[1,4,7,8]

Catalysts based on thermally stable high-silica zeolites of the ZSM-5 type with the introduced Pd, Co, and Mn ions can be promising for the high-temperature oxidation of hydrocarbons.[9] The presence of the above ions in the zeolite matrix as isolated species can prevent the metal agglomeration and sintering of the catalyst.

In this work, the stability of the Pd-, Co-, and Mn-zeolite catalysts under reaction conditions in the high-temperature methane oxidation was studied.

Experimental

High-silica zeolite TsVM (ZAO Nizhegorodskii sorbent, Si/Al = 20) was used for the preparation of the Mn- and Co-zeolite catalysts, and zeolite ZSM-5 («PQ Corporation», Si/Al = 25) was used for the preparation of the Pd-containing catalyst. To introduce a metal, the starting zeolite in the ammonia form was impregnated to incipient wetness with aqueous solutions of the $Mn(NO_3)_2$ and $Co(NO_3)_2$ salts and a Pd-aminonitrile complex. Samples obtained were dried in air for 6 h at 20 °C, 4 h at 140 °C and then calcined for 2 h at 500 °C in an air flow. The catalysts 3% Mn/ZSM-5, 2% Co/ZSM-5, and 1% Pd/ZSM-5 were prepared according to the above procedure. It is believed[10—13] that the metal ions in the catalysts of the above compositions are present in the isolated state.

To produce the block catalysts, the metal-containing zeolites were supported on a foil of the thermally stable Fe—Cr—Al alloy with a thickness of 80 μm. Both the smooth and corrugated zeolite-covered sides of the foil were laid together and turned to a roll with a height of 2.6 cm and a cross-section area of 4.1 cm^2. The blocks prepared had 40 triangle channels per 1 cm^2 of a cross-section. The metal content in zeolite in the above blocks was 0.06—0.07 g. The block weight was 5.22 g.

Complete methane oxidation was carried out at atmospheric pressure in a flow setup with a gas feed rate of 10—1900 cm^3 min^{-1}. The initial air mixture contained 2.5 vol.% CH_4. The products were analyzed by GC on a column packed with Polysorb-1 (thermal conductivity detector, helium as a carrier-gas, temperature 25 °C). No products except CO_2 and H_2O were found in the gas phase. The methane conversion in the runs was estimated from the amount of CO_2 formed. The setup and the procedures for catalyst preparation and activity measurement were described earlier.[9]

The activity was measured at 500, 550, 600, 650, and 700—720 °C over the following catalysts: (1) a freshly prepared catalyst; (2) a catalyst tested after runs at 720 °C followed by cooling to 500 or 600 °C; (3) a catalyst tested after repeated runs at 720 °C; (4) a catalyst after heating for 0.5 h at 800 °C; (5) a catalyst heated for 0.5 h at 900 °C. Cooling and heating of the catalyst were performed in a flow of the reaction mixture without its unloading from the reactor.

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The activation energy for the heterogeneous catalytic methane oxidation was calculated from the temperature dependence of the initial mixture feed rate (V) at a conversion (α) of 30%.[14] The activation energy of the heterogeneous-homogeneous methane oxidation was determined from the temperature dependence of the contact time (τ) at which the reaction is drastically accelerated. This procedure is widely used in studies of the kinetics of homogeneous reactions.[15,16]

The contact time for the metal block zeolite catalysts was determined as the ratio between the volume of the catalyst block and the initial mixture feed rate. The initial mixture feed rate at the specified conversion was taken as a measure for the catalytic activity (A).[17] The activity was calculated according to the formula

$$A = V\alpha C/22.4m_M,$$

where C is the methane concentration in the initial mixture and m_M is the concentration of a transition metal in the catalyst.

Results and Discussion

In our previous work,[9] we found that two processes contribute to the complete high-temperature methane oxidation over the zeolite catalysts containing the Pd, Co, and Mn isolated ions: heterogeneous-catalytic and heterogeneous-homogeneous. The first process predominates at small contact times and low CH_4 conversions (≤50%). Under these conditions, methane conversion gradually increases with increasing τ, while in the heterogeneous-homogeneous process, slight changes in the contact time result in a sharp, jump-like approach to the complete methane conversion to CO_2.

Methane oxidation over catalyst 1% Pd/ZSM-5. Complete oxidation of CH_4 over the catalyst 1% Pd/ZSM-5 supported on the metal block was studied at 500—720 °C and conversions of 10—100% (Figs 1, 2; Table 1). In the heterogeneous-catalytic process, the starting catalyst has a stable reproducible activity when the contact time is varied from 2 to 40 s and the temperature is varied in the range of 500—600 °C. The catalyst activity decreases three times when the temperature of the catalyst in the reaction medium increases to 650 °C for 0.5 h. Accordingly, the activation energy of the heterogeneous-catalytic process calculated for the deactivated catalyst increases from 84 to 117 kJ mol^{-1}. All the following treatments of the catalyst in the reaction medium at 720, 800, and 900 °C do not change the catalyst activity. As can be seen from the results shown in Fig. 2, the reaction rate at 600 °C for catalysts treated at 720—900 °C remains unchanged in all the runs.

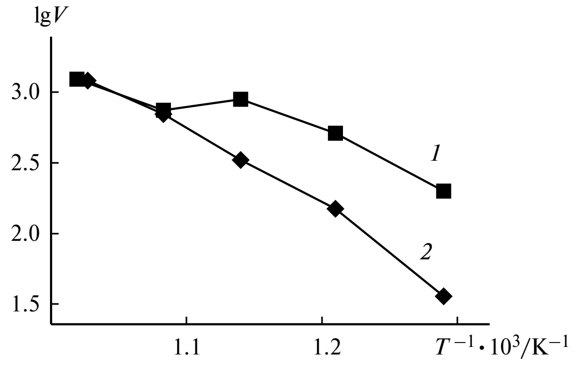

Fig. 1. Plot for the lg V *vs.* inverse temperature in complete methane oxidation for the metal block catalyst 1% Pd/ZSM-5: starting catalyst (*1*) and catalyst after the first heating at 720 °C and following heatings up to 900 °C (*2*).

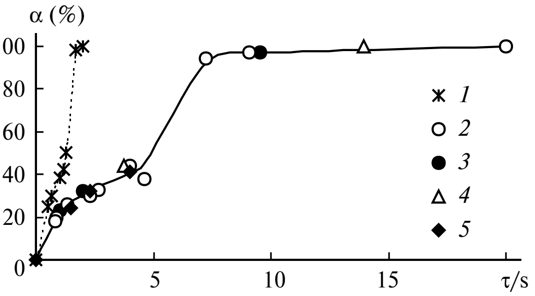

Fig. 2. Effect of the treatment temperature of the metal block catalyst 1% Pd/ZSM-5 on the pattern of dependence of conversion (α) on contact time (τ) in methane oxidation at 600 °C: starting catalyst (*1*), catalyst after the first heating (*2*) and the second heating (*3*) at 720 °C, after heating at 800 (*4*) and 900 °C (*5*).

Deactivation of the Al_2O_3-based palladium catalysts at temperatures above 600 °C is well known.[1—8] The deactivation occurs continuously during the run and upon increasing the reaction temperature. One of the reasons for deactivation is a decrease in the active phase dispersion and an increase in the sizes of the crystals of platinum and palladium oxides. A feature of deactivation of the metal block-supported catalyst 1% Pd/ZSM-5 at 650 °C is that a short time (0.5 h) is needed to effect the activity decrease. The further catalyst calcination in the reaction environment from 650 to 900 °C has no effect on

Table 1. Maximum temperature of stable performance of catalysts (T_{max}) and their activity (A) in complete methane oxidation at 500 °C and 33% conversion

Catalyst	A/mol (g metal h)$^{-1}$	T_{max}/°C
1% Pd/ZSM-5 [a]	4.4	650
1% Pd/ZSM-5 [b]	1.2	900
3% Mn/ZSM-5	0.12	720
2% Co/ZSM-5	0.029	800
10% Pd/Al_2O_3 [c]	0.35	600
0.3% Pt/Al_2O_3/Ni [d]	0.17	1000

[a] Starting catalyst.
[b] Deactivated catalyst.
[c] See Ref. 8.
[d] See Ref. 20.

the activity of the catalyst, which operates steadily for 12 h. The activity of the starting catalyst 1% Pd/ZSM-5 deteriorates in the course of methane oxidation at 650 °C probably due to a change in the Pd ion coordination caused by zeolite dehydration.

Similar decline in activity is observed for the catalyst Cu/ZSM-5.[18] Its activity in methane oxidation sharply decreases after the catalyst was calcined at 800 °C, and this is due to a change in the coordination of Cu ion from the octahedral to square pyramidal. The amount of the isolated copper ions in the catalyst remains the same as before calcination. No decline of the activity in the repeated runs was found.

An increased stability of the catalyst 1% Pd/ZSM-5 is likely due to the fact that the concentration and state of the isolated palladium ions in the zeolite do not change upon calcination at temperatures above 650 °C.

The effect of thermal treatments of the catalyst on the homogeneous-heterogeneous methane oxidation manifests itself in that the contact time corresponding to the onset of the homogeneous-heterogeneous process at 600 °C increases from 1.5 to 5 s (see Fig. 2). The activation energy calculated for conversions close to 100% on both the starting and calcined catalysts was 156±5 kJ mol^{-1}.

Table 1 compares the activity and time-on stream behavior of the Pd-zeolite catalysts with the analogous parameters of the earlier studied catalysts 10% Pd/Al_2O_3 and 0.3% Pt/Al_2O_3/Ni.[19,20] The feed rate of the working mixture at the specified percent of its conversion to the reaction product was taken as the activity value.[17] This value, which is proportional to the reaction rate constant, can be referred to 1 g of the active component of the catalyst, specifically to 1 g of palladium. It is noteworthy that the specific activity of the catalyst 1% Pd/ZSM-5 stabilized after thermal treatment is several times higher at 500 °C and the 33% methane conversion than those of the aluminopalladium[19] and aluminoplatinum[20] catalysts.

Methane oxidation over catalyst 2% Co/ZSM-5. Complete oxidation of CH_4 was studied over the metal block-supported catalyst 2% Co/ZSM-5 at 650—720 °C and conversions from 5 to 100%. After the runs over the freshly prepared catalyst at 720 °C,[9] the catalyst was cooled to 650 °C in the reaction mixture flow and its activity measured. The activity values coincided exactly with those obtained over the starting catalyst (Fig. 3). However, after calcination in the working mixture flow at 900 °C, the catalytic activity considerably decreased; at a conversion of 18% the reaction mixture feed rate decreased from 600 to 350 $\mathrm{cm}^3\ \mathrm{min}^{-1}$ and the catalyst showed a stable performance in a three-hour run.

The activity decline in the homogeneous-heterogeneous process is displayed in an increase in the contact time corresponding to the onset of the heterogeneous-homogeneous process from 1.5 to 2.4 s (see Fig. 3).

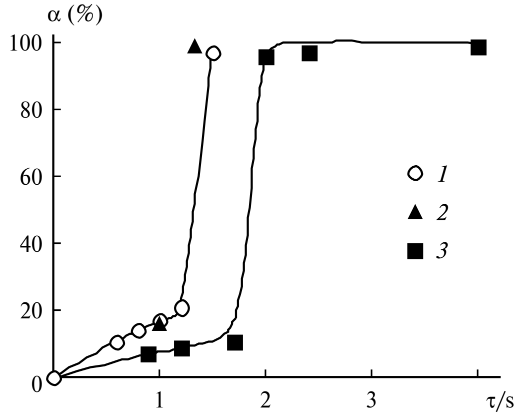

Fig. 3. Methane conversion (α) *vs.* contact time (τ) at 650 °C over the metal block-supported catalyst Co/ZSM-5: starting catalyst (*1*), catalyst after heating at 720 (*2*) and 900 °C (*3*).

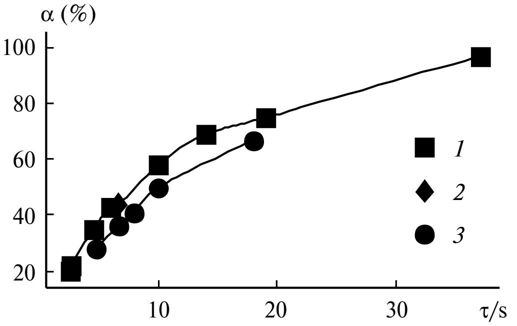

Fig. 4. Methane conversion (α) *vs.* contact time (τ) at 600 °C over the metal block-supported catalyst 3% Mn/ZSM-5: starting catalyst (*1*), catalyst after heating at 670 (*2*) and 720 °C (*3*).

Methane oxidation over catalyst 3% Mn/ZSM-5. Complete oxidation of CH_4 to CO_2 was studied over the metal block-supported catalyst 3% Mn/ZSM-5 in the temperature range 500—720 °C at conversions 8—99%.[9] After the run at 670 °C, the temperature was decreased to 600 °C and the repeated runs were conducted. The methane conversions obtained coincided exactly with the initial values for the starting catalyst,[9] indicating its high stability in the temperature range under study (Fig. 4). When the temperature of the catalyst treatment in the reaction medium was increased to 720 °C, the activity somewhat decreased.

The specific activity of the Mn-catalyst is 10 times and that of the Co-catalyst is 40 times lower than the specific activity of the calcined Pd-catalyst (see Table 1).

Hence, among the zeolite catalysts under study, the catalyst 1% Pd/ZSM-5 is most efficient with respect to both the time-on stream behavior and activity in high-temperature methane oxidation. It is likely that the Pd ions in the catalyst heated in the reaction medium (as well as in the starting catalyst) are isolated ions, although their coordination sphere could undergo some transformations.

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