The MnOₓ-Al₂O₃ catalysts in the reaction of C₁-C₃ hydrocarbons deep oxidation

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Abstract. The effect of the amount of Mn (II) in the precursor of manganese-aluminium oxide catalysts for the complete oxidation of hydrocarbons on the phase composition and kinetic parameters of the reaction was studied. It was shown that an increase in the amount of manganese in the catalysts results in an increase in the constants of C₁-C₃ hydrocarbons oxidation reaction rates. An increase in the number of carbon atoms in the alkane leads to an increase in the reaction rate and a decrease in the energy of reaction activation. Promising catalysts for the catalytic combustion of hydrocarbons were identified.

1. Introduction
Deep catalytic oxidation of hydrocarbons has a distinct advantage over flame combustion. The temperature of combustion is lower as compared to flame combustion, respectively, the efficiency of heating plants is higher, there is a possibility of poor gas-air mixtures after-combustion, and the amount of emissions of incomplete oxidation products and nitrogen oxides polluting the atmosphere is significantly lower [1, 2]. The most common catalysts for the deep oxidation of hydrocarbons are systems containing noble metals [1, 3, 4], which are highly active at low temperatures. Catalysts containing noble metals have several disadvantages: high cost, active metal poisoning with sulphur compounds, active phase sintering. Systems containing transition metal oxides – nickel, copper, chromium, cobalt, and manganese – as the active phase applied to heat-resistant carriers [2, 5-8] are being studied as possible alternative catalysts for the oxidation of hydrocarbons. Often, pure or promoted aluminium oxide with manganese oxides applied to obtain thermally stable hydrocarbon combustion catalysts [2, 9] is used as a carrier of the active phase.

According to [1, 4], the thermal stability of reactors and exothermic reaction modes are determined by the design of reactors and process specifics: a fixed or boiling catalyst bed, stationary mode or reverse process. But the main factor in addition to the chemical composition of reaction gases, which determines the thermal effect of the oxidation reaction, is the catalyst used and the kinetics of the reaction behaviour. Today patterns of the oxidation of many individual substances and mixtures have been determined, the impact of the size effect of the active component or the method of catalyst preparation on the specific catalytic activity has been shown [1, 3, 4, 7], the impact of the nature of the oxidized substance on the kinetics of oxidation has been considered. Today the effect of the amount of the active component in the catalyst on the patterns of deep oxidation of methane and its higher homologs has not been studied as much as possible.
The purpose of the work is to study the effect of the amount of Mn (II) in the precursor of nanofiber aluminium oxyhydroxide MnO₅-Al₂O₃ catalysts on the phase composition and patterns in the reaction of deep oxidation of C₁-C₃ alkanes.

2. Experimental Part
The method for producing nanofiber aluminium oxyhydroxide is based on the reaction of aluminium nanopowder oxidation with water [9]. Aluminium nanopowder obtained by the method of electric explosion of a conductor in argon with the addition of oxygen in the amount of 0.05 g per 1 g of aluminium wire was used as the initial material. Such conditions make it possible to obtain passivated powders containing active aluminium in the amount of min. 85% wt. The synthesis and modification of AIOOH nanofibers were carried out in an aqueous solution of a manganese sulfate salt with different concentrations of manganese ions in the solution. A detailed procedure for the preparation of modified specimens of aluminium oxyhydroxide was described in [9] and consists in AIOOH nanofibers growth and modification processes conducted simultaneously. To obtain AIOOH nanofibers with different amounts of manganese ions, the concentration of the aluminium nanopowder used for synthesis was kept constant at 0.375 mg/L, and the amount of Mn²⁺ ions in the solution was changed from 1.0 to 1000 mg/L.

The quantitative content of manganese ions in the modified nanofibers was determined by chemical analysis using Agilent 4100 microwave plasma-atomic emission spectrometer. The phase composition of the specimens was determined using MiniFlex 600 X-ray (Rigaku) diffractometer and CuKα radiation (λ=1,5418 Å). Scanning conditions: the scanning speed – 2 deg/min, the range of scanning angles 2Θ – from 10° to 100°.

The catalytic properties of the specimens were studied in the flow-through mode with a fixed-bed catalyst, a U-shaped quartz reactor with an inner diameter of 4·10⁻³ m, and a catalyst fraction of 0.315-0.4·10⁻³ m. For the purpouses of activation the specimens were precalcinated in air at a temperature rise of 10°C/min from 20 to 850°C and held at T=850°C for 1 hour. Dosing and mixing of gases were carried out using FGP Chromatec Crystal gas flow generator. The reaction mixture consisted of a hydrocarbon – 0.5 vol. %, O₂ – 13.0 vol. %, the rest was N₂, the contact time was 0.1 s, T=300-800°C [10]. Natural gas containing methane 93.0 vol. %, ethane 4.2 vol. %, propane 2.1 vol. %, the rest was CO₂ and N₂ was oxidized using a flow-through reactor with an inner diameter of 10·10⁻³ m, contact time 0.4 s, oxygen excess coefficient α=1.1.

The analysis of the source gases and reaction products was chromatographic. For the purposes of analysis, we used Crystal 5000.1 gas chromatograph (Russia) with two heat conductivity detectors and a flame ionization detector. The following chromatographic columns were used to separate the gas mixture: 1) a 4 m packed column with NaX sorbent (60/80 mesh) for the separation and determination of oxygen, nitrogen, methane, and carbon monoxide (Ar carrier gas); 2) a packed column 1.5 m long with Carbosieve S-II sorbent (60/80 mesh) for the detection and calculation of carbon dioxide concentration (He carrier gas); 3) HP-PLOT Al₂O₃(KCl) capillary column with a length of 50 m for the separation and determination of C₁-C₅ hydrocarbons. The temperature of the column thermostat was 80°C. The concentration of gas mixture components was calculated by the absolute calibration method using Chromatec Analytic 2.5 software [5].

The activity of the catalyst was characterized by the rate of hydrocarbon oxidation calculated by the reaction first order relative to the hydrocarbon [10] for the plug-flow reactor:

\[ W_{hc} = \frac{C_{hc} \cdot U}{m \cdot S_{sp}} \cdot \ln \frac{1}{1-X} \left[ \frac{mol}{m^2 \cdot s} \right], \]

where \( C_{hc} \) is the relative molar concentration of the hydrocarbon (mol/mol), \( U \) is the molar flow under normal conditions (mol/s), \( m \) – the weight of the catalyst (g), \( S_{sp} \) – the specific surface area (m²/g), \( X \) – the degree of hydrocarbon conversion.
3. Results and Discussion

The amount of Mn$^{2+}$ in precursors has a significant effect on the final phase composition of calcinated catalysts. As a result of X-ray phase analysis only $\gamma$-Al$_2$O$_3$ phase was found in specimens I-II (Figure 1), where the amount of manganese was low. An increase in the manganese content up to 3.2\% in the precursor (specimen No. III, Fig. 1) resulted in the development of two forms of aluminium oxide during calcination – $\gamma$-Al$_2$O$_3$ and $t$-Al$_2$O$_3$ and manganese-alumina spinel. Specimen No. IV after thermal exposure contained MnAl$_2$O$_4$ spinel and non-stoichiometric by oxygen $\sigma$-Al$_2$O$_3$. In the case of specimen No. V containing the maximum amount of manganese, according to X-ray phase analysis data, the catalyst consisted of $\alpha$-Al$_2$O$_3$ and manganese oxides Mn$_2$O$_3$ and Mn$_3$O$_4$. The specific surface of the specimens calcined at $T=850^\circ$C decreased as far as the amount of manganese in the catalyst precursor (see the Table below) increased from 189 to 15 m$^2$/g.

![Figure 1. Data on the XPA of manganese-containing systems. The contents of Mn, wt \%, are (I – 0.9, II – 1.5, III – 3.2, IV – 5.7, and V – 10.5; (1) $\gamma$-Al$_2$O$_3$, (2) $t$-Al$_2$O$_3$ (cub.), (3) $\gamma$-Al$_2$O$_3$, (4) MnAl$_2$O$_4$, (5) $\sigma$-Al$_2$O$_3$, (6) $\alpha$-Al$_2$O$_3$, (7) Mn$_2$O$_3$, and (8) Mn$_3$O$_4$)](image-url)
The dependence of the rate of C₁-C₃ alkanes oxidation on the manganese amount in the catalyst is given in the Table. The oxidation reaction rate increased as far as the length of the hydrocarbon chain increased. These results correspond to the data of other authors, according to which the rate of alkane oxidation increases as far as the carbon chain length in the molecule increases [1, 3]. An increase in the rate of hydrocarbons oxidation is due to the fact that the stage that determines the speed of the process is the breaking of the first C-H bond [1], the strength of which decreases as far as the length of the hydrocarbon molecule increases.

An increase in the amount of manganese in the catalysts results in an increase in the rate of C₁-C₃ hydrocarbons oxidation. The specimen containing manganese in the precursor in the amount of 10.5% wt. at T=420°C is characterized by the maximum rate of hydrocarbons complete oxidation (see the Table below) and the minimum energy of hydrocarbons deep oxidation reaction activation.

**Table 1.** Dependence of the hydrocarbon oxidation rate (W), energy of C₁-C₃ hydrocarbons oxidation reaction activation (Eₐ) and specific surface area (Sₛₚ) on the amount of Mn²⁺ in the precursor.

| No. | Amount of Mn²⁺ in the precursor, % wt. | Sₛₚ of the catalyst (Tₑₙₐ₅=850°C), m²/g | CH₄  | C₂H₆  | C₃H₈  |
|-----|-------------------------------------|--------------------------------------|------|-------|-------|
|     |                                     |                                       | W, 10⁶ mol/m²·s | Ea, kJ/mol | W, 10⁵ mol/m²·s | Ea, kJ/mol | W, 10⁴ mol/m²·s | Ea, kJ/mol |
| 1   | 0.9                                 | 189                                  | 0.010 | 123.6 | 0.016 | 104.1 | 0.006 | 90.3 |
| 2   | 1.5                                 | 177                                  | 0.064 | 112.9 | 0.018 | 103.3 | 0.008 | 86.0 |
| 3   | 3.2                                 | 128                                  | 2.464 | 103.2 | 0.152 | 102.5 | 0.019 | 81.9 |
| 4   | 5.7                                 | 28                                   | 2.370 | 93.6  | 1.170 | 90.9  | 0.461 | 80.1 |
| 5   | 10.5                                | 15                                   | 3.540 | 83.9  | 2.770 | 82.5  | 1.600 | 79.1 |

It was discussed in [2, 10] that high-temperature MnOₓ/Al₂O₃ catalysts are not inferior by some parameters to catalysts based on noble metals. The rates of methane and ethane oxidation calculated based on the data given in [3] using 0.8% Pt/Al₂O₃ catalyst under close conditions (0.5% vol. hydrocarbon in air) at T=420°C with Pt particle size of about 3 nm or more correspond to the oxidation rates of 10.5% MnOₓ/Al₂O₃. From a practical perspective, especially for exothermic, high-temperature hydrocarbon combustion processes, initially highly active platinum catalysts with highly dispersed platinum can reduce their activity [1, 4, 11]. Hüttig characteristic temperature, above which the surface mobility of atoms in the applied metal is observed, corresponds to 0.3·Tₘₑₙₜ (Tₘₑₙₜ is the melting point of the metal according to the absolute temperature scale), respectively, for the applied Pt Hüttig temperature is ~ 340°C [4]. Therefore, in case of using the catalyst above this temperature in a redox environment for a long time, nanoparticles of platinum will unite, and the activity will decrease.
Figure 2. Dependence of hydrocarbon conversion (C) (1, 2 – propane; 3, 4 – ethane; 5, 6 – methane) on temperature (catalysts: 5.7 wt. % Mn (II) – 2, 4, 5; 10.5 wt. % Mn (II) – 1, 3, 6)

If we consider catalytic oxidation of natural gas (a mixture of C1-C3 hydrocarbons) with the oxygen excess coefficient of α=1.1 (α=1.0 corresponds to stoichiometry for deep oxidation reaction) using catalysts No. 4 and No. 5 (see the Table above), a noticeable oxidation of propane starts with a temperature of 250°C, ethane – 350-400°C, and methane – 500°C (Figure 2). The run of the conversion curves from the temperature for hydrocarbons with different hydrocarbon chain lengths corresponds to a certain oxidation activation energy. It means that a decrease in the reaction activation energy results in a decrease in the temperature of the oxidation reaction (Figure 2) [1, 3]. Figure 2 shows that the conversion of ethane and propane in the case of a catalyst containing 10.5% wt. manganese at the same temperature is higher as compared to catalyst No. 5. In the case of methane, another dependence is observed: over the entire temperature range from 350 to 600°C the conversion of methane with 5.7% Mn catalyst is higher as compared to a system containing 10.5% manganese. At a reactor temperature of 600°C, the methane conversion for the 5.7% system was 88.1% versus 69.3% for the catalyst containing 10.5% Mn (Fig. 2). A further increase in the temperature results in a transition of the reaction mode to almost adiabatic (autothermal) mode of catalytic combustion [1, 4, 11].

4. Conclusion
Therefore, during oxidation of real natural gases the transition to the autothermal mode of both catalysts occurs at approximately the same temperature; accordingly, these systems can be effectively used as catalysts for thermal convectors. In practical application, a system containing 10.5% manganese is more promising as a catalyst for the combustion of hydrocarbons. Unlike the catalyst containing 5.7% Mn, where aluminium oxide is in the metastable form (α-Al2O3), the catalyst containing 10.5% manganese also contains a thermodynamically and thermally stable α-Al2O3 phase in its structure, which is important when conducting a high-temperature process – catalytic combustion of hydrocarbons.

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