Nano-sized polyoxide and low percentage Pt-Ru catalysts for production of synthesis-gas

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Studying of genesis of the Ni-Cu-Cr/2%Ce/(θ+α)-Al₂O₃ catalyst for receiving of synthesis-gas was carried out with using of physical and chemical methods. Optimum conditions for preparation of the catalyst for carrying out selective catalytic oxidations (SCO) of methane to synthesis-gas have been determined: impregnation of the modified carrier by water solutions of metal nitrates, drying, and calcination on air at 873 К during 1 h, at 1173 K during 1 h and reduction in H₂-Ar mixture during 1 h at 1173 K. It was shown, that nano-sized particles of Ni, Cu oxides and their mixtures (d = 20-100 Å) are formed during genesis. CeO₂ and larger mixed oxides of Ni with Cr, Ce with Cu, Cu with Cr and Ni and Cu aluminates are formed after high-temperature heating of catalyst. Under the action of H₂ at 1173 K Cu and Ni oxides are reduced up to nano particles of Ni₀, Cu₀, and their alloy NiCu₃.₈ (d = 2.08; 1.08; 1.27 Å) as a friable polycrystalline film. There are also translucent particles of Ce₆O₁₁ (50-60 Å) and larger dense mixed phases on a surface of formed α-Al₂O₃. That phase structure of the catalyst is kept during application in selective oxidation of methane into synthesis-gas. The fact of transformation of the Ni and Cu aluminates into metal particles and formation of NiCu₃.₈ clusters under the action of H₂ and CH₄ are confirmed by TPR and TEM with micro diffraction of electrons. The leading part in reducing decomposition of Ni(Cu)Al₂O₃ carries out, probably, copper which is reduced and oxidized more easily, than nickel and other elements.

The optimum conditions of selective oxidation of CH₄ in the diluted mixes (CH₄+O₂+Ar) with formation of synthesis-gas were determined during investigation the influence of some parameters on reduced Ni-Cu-Cr/2%Ce/(θ+α)-Al₂O₃ catalyst: T = 1173 K, CH₄:O₂ = 2, τ = 2.35-3.27 ms (W = 1.53-1.17·10⁶ h⁻¹) with α.CH₄ = 88-100% and selectivity by CO = 99.6-100%, H₂ = 99-100% with formation of CO₂ traces (0.005%). The catalyst has worked 56 hours without decrease of activity and formation of carbon on a surface. It indicates on prospect of its further investigation, on stability in SCO with application of more concentrated mixes of CH₄ with others alkanes both with O₂, and in combined processes of SCO with steam conversion with use of porous block carriers from cordierite and metal alloys. SCO process proceeds selectively up to H₂ and CO without formation of CO₂. It indicates on course the reaction by dissociated adsorption of CH₄ on Ni₀, on NiCu₃.₈ clusters up to carbon and atomic hydrogen which is dissolved in NiCu₃.₈ alloy. According to TPO and TPD of oxygen, activation of oxygen for interaction with carbon can be carried out on Cu₀, Ni₀, and also NiCu₃.₈ clusters. It is possible, that there is a division of functions in activation of components: CH₄ - on Ni atoms, O₂ - on Cu atoms, and also on Ce₆O₁₁.

0.5%Pt-0.5%Ru/2%Ce/(θ+α)-Al₂O₃, reduced by H₂ at 1173 K, presents a mixture of Pt and Ru (3-30 nm) nanoparticles in reduced and partially oxidised condition surrounded by bigger formations of surface compound CeAlO₃ with perovskite structure and oxide Ce₆O₁₁ (15-80 nm). High conversion of CH₄ and selectivity by CO and H₂ (close to 100%) at short contact times (2.35-8·10⁻³ s) are observed by using of that catalyst in catalytic partial oxidation of CH₄ to synthesis-gas at 1173 K and atmospheric pressure. Methane is activated on Pt and Ru metal clusters while oxygen is activated on Ce oxide nanostructures.

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