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STABILITY OF PLATINUM-RUTHENIUM CATALYSTS IN THE SELECTIVE SYNTHESIS OF H_2 AND CO

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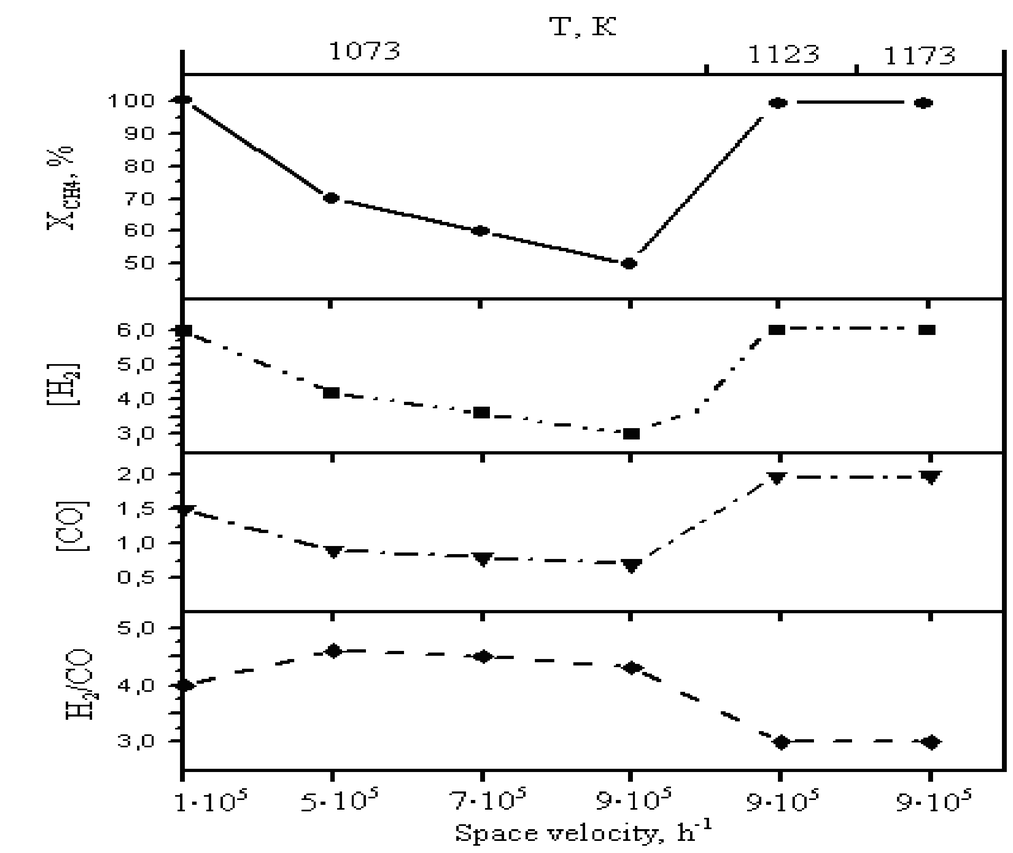
INTRODUCTION. Synthesis gas is the main raw material for producing a wide range of petrochemical products. Correlation of the ratio of H_2 and CO in the composition of synthesis gas makes it possible to obtain liquid hydrocarbons or oxygenates, CH_3OH, CH_3COOH, CH_2O and C_2H_6O. The process of SCO of methane which proceeds with a molar ratio of hydrogen to carbon monoxide equal to 2.0, could become a reaction, an alternative reaction of steam reforming of methane for the production of synthesis gas. An alternative reaction of steam reforming of methane to obtain syngas can be the process SCO of methane which proceeds with an optimal molar ratio of hydrogen to carbon oxide equal to 2.0.

This paper presents data on the stability of the developed Pt-Ru = 1 : 1 (Pt : Ru = 0.7 : 0.3 at.%) catalyst. The activity of the catalyst was studied in the reactions of selective catalytic oxidation (SCO) and steam oxygen conversion (SOC) of methane into synthesis gas at low contact times. As a result of the conducted research, the methods of catalyst regeneration were determined.

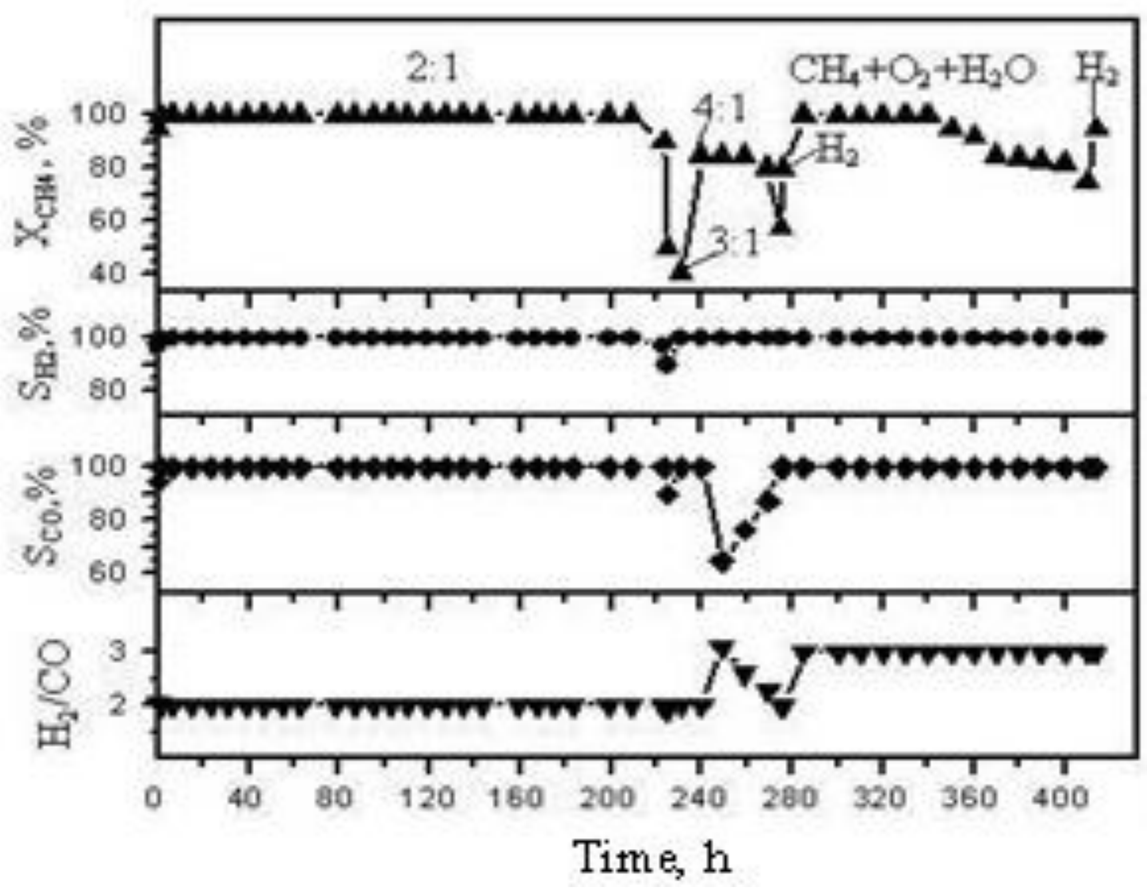
Experimental. Pt-Ru catalysts supported on 2%Ce/(θ+α)-Al_2O_3 have been prepared by incipient wetness on (θ+α)-Al_2O_3 (100-200 μm, S = 57.7 m^2/g) from water solutions of salts with subsequent heating and reduction with H_2+Ar at 623-1023 K. Tests were carried out in a continuous flow quartz micro reactor by a literature technique.

The activity of the developed catalytic systems in the process SCO of methane was determined in a catalytic flow unit at atmospheric pressure in a quartz microreactor with an internal diameter of 0.45 cm. 10 mg of the catalyst suspension was thoroughly mixed with quartz powder (particle size 0.2 mm in a ratio of 1: 43, height 20 mm). Then, larger quartz particles (1÷2 mm) were added to the reactor from above to a total layer height of 70 mm. After that, the initial reaction mixture was fed under the following conditions: CH_4:O_2:Ar = 2.0 : 1.0 : 97.0. (%) T = 1173K, V = $9\cdot10^5$ h^{-1}, τ = 0.004 s. In the process the SOC of methane: CH_4 : O_2 : H_2O : Ar = 2.0 : 1.0 : 2.0 : 95.0, %, T = 1073 – 1173 K, V = $1\cdot10^5$ - $9\cdot10^5$ h^{-1}.



Experimental conditions: SOC of CH_4 : O_2 : H_2O : Ar = 2.0 : 1.0 : 2.0 : 95.0.%, T = 1073 – 1173 K, V = $1\cdot10^5$ - $9\cdot10^5$ h^{-1}

Figure 1 - Influence of the volume velocity on change of X_{CH4}, [H_2], [CO] in the SOC of methane by 1.0%Pt-Ru (1:1)/ 2%Ce/(θ+α)-Al_2O_3

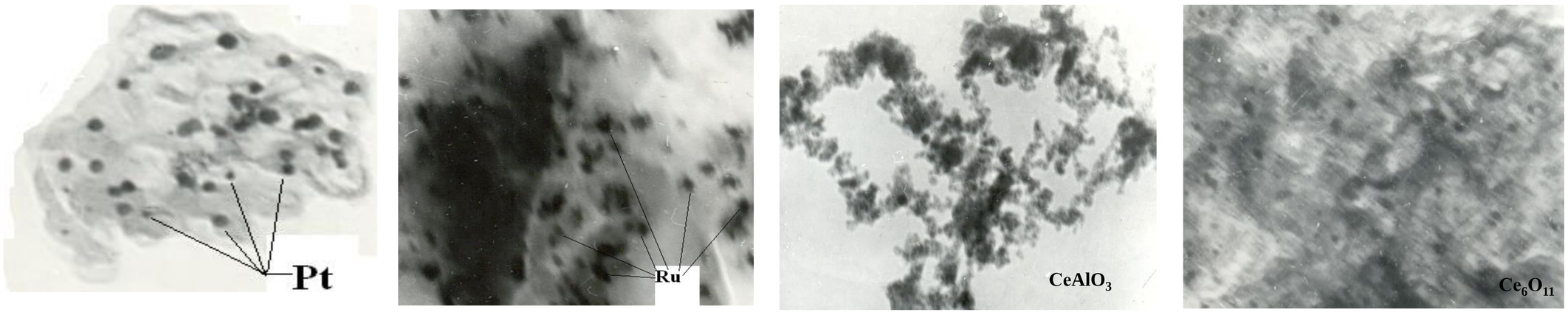


Condition the process of SCO of methane: CH_4 : O_2 : Ar = 2.0 : 1.0 : 97.0, %, T = 1173 K, V = $9\cdot10^5$ h^{-1}, τ = 0.004 s and SOC of methane CH_4 : O_2 : H_2O : Ar = 2.0 : 1.0 : 2.0 : 95.0, %, T = 1073 K, V = $1\cdot10^5$ h^{-1}, τ = 0.036 s

Figure 2 – Change conversion of methane, selectivity of H_2 and CO, ratio of H_2/CO on 1.0 % Pt-Ru (1:1)/2%Ce/(θ+α)Al_2O_3 catalyst in time

Thus, determined that the process of SOC of methane with the optimum ratio of CH_4 : H_2O = 1 : 1 proceeds with complete conversion of the initial methane and maximum selectivity for the main products of the reaction without formation of CO_2 at 1123 K and volume velocity of $9\cdot10^5$ h^{-1} and decreasing the temperature of the reaction to 1073 K and volume velocity of $1\cdot10^5$ h^{-1} on 1.0%Pt-Ru (1:1)/ 2%Ce/(θ+α)-Al_2O_3 catalyst.

Thus, it is established that the developed catalytic system 1.0%Pt-Ru(at. %)/2%Ce/(θ+α)-Al_2O_3 selectively works without losing its activity for 414 hours in the reaction of SCO and SOC of methane into synthesis gas.



Conclusion

During the study of the stability of a low-percentage granular sample of 1.0% Pt-Ru/2% Ce/(θ+α)Al_2O_3 catalytic system in the process of oxidation of methane, regeneration methods were found that allow stable conduct of the process of SCO and SOC of methane for 410 hours. As a result of the process, a synthesis gas was obtained with a ratio of H_2/CO = 2.0 without the formation of CO_2, which is most suitable for its use in the Fischer-Tropsch synthesis of methanol and hydrocarbons. It is assumed that the reaction of SCO of CH_4 proceeds by a direct mechanism involving reduced Pt^0, Ru^0 and Pt-Ru nanoclusters detected by TEM research after testing the stability of the developed Pt: Ru (1:1) catalyst on a carrier. Pt-Ru/2%Ce/(θ+α)-Al_2O_3, reduced in H_2 at 573K and 1173K, represents as nanoparticles of Pt° and Ru° (5-30 nm) in the reduced and partially oxidized condition, surrounded by smaller formations of $CeAlO_3$ surface compounds and Ce_6O_{11} (3-10 nm) oxides. Presence of phases of the Pt-Ru alloy and $Pt_{13}Ru_{27}$ intermetallic compounds is possible because there are 3 basic lines at sets of interplanar distances of the mixed phases calculated on parameters of elementary cell.