



Nanostructured supported Pt-, Ru- and Pt-Ru catalysts for oxidation of methane into synthesis-gas

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ABSTRACT

Mono- and bimetallic Pt-, Ru- and Pt-Ru catalysts with various Pt to Ru ratio for process of selective catalytic oxidation of methane to synthesis-gas at short contact time are developed. Precious metals were supported on alumina which was modified by cerium to enhance dispersion over carrier. Pt-Ru/2%Ce/($\theta + \alpha$)-Al₂O₃, reduced by H₂ at 1023 K, presents a mixture of nano-particles of Pt⁰ (7.5–15.0 nm), Ru⁰ (5.0–30.0 nm), its alloy in the mixed catalysts and intermetallic compounds of Pt₁₃Ru₂₇ (3.0 < *d* < 18.0 nm). Semi-transparent Ce₆O₁₁ particles (3.0–10.0 nm) and CeAlO₃ (3.0–5.0 nm) are present on the surface of Al₂O₃. Such phase composition provides for optimum selective oxidation of CH₄ to synthesis-gas.

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1. Introduction

One of the major problems in the field of organic catalysis is activation of CH₄ for purposeful one-step production of organic compounds and fuel compositions by means of new nano-cluster catalysts. Highly active and thermostable Rh, mixed Pt-Pd-Rh, and Pt-LaNiO₃ nanostructural catalysts on porous block ceramic and metal carriers can be used for processing of natural CH₄ into synthesis-gas and others H₂-containing mixtures with the subsequent application in various processes: for synthesis of methanol, in gas turbines as the basic fuel and additives to gasoline for cars, etc. [1–4]. There are data on application of Ru or mixed Pt-Ru catalysts in processes of oxidative conversion of CO and organic substances. So, the behavior of Ru catalysts on Al₂O₃ was studied in oxidation of CO [5]. It was shown that there was a slow decrease of activity of the catalyst due to oxidation of Ru by O₂ of a reaction mixture at temperatures below 473 K. The deactivated catalyst was activated by reduction with H₂. By using the 0.26% Pt-Ru (1:1) catalyst over θ -Al₂O₃, promoted by cerium, a complex purification was performed of exhaust gases like CO, NO, and hydrocarbons [6]. Selective catalytic oxidation of CH₄ (SCOM) into synthesis-gas was studied on 1% Ru, 1% Pt, and 1.3% (Ru, Pt) on γ -Al₂O₃ catalyst [7]. It was shown that reaction performed consequently in two stages on Pt or Pt-Ru catalysts. At the first stage at rather low temperature (673 K) there is a complete oxidation of CH₄, and synthesis-gas was received at

the second stage when proceeds reforming of residual CH₄ with CO₂, H₂O at more high temperature (~1073 K). We investigated earlier [8,9] the reaction of SCOM on 1% (0.5%Pt+0.5%Ru) catalyst over ($\theta + \alpha$)-Al₂O₃, promoted by 2%Ce. It has been shown high conversion of CH₄ and selectivity of CO and H₂ (up to 100%) formation (*S*_{CO}, *S*_{H₂}) in reaction of SCOM at short contact time (2.4–8.0 ms). From the works with using of mixed Pt-Ru catalysts a specific optimum ratio of noble elements in catalysts and their concentration on carriers were not determined.

The purpose of our work was to study the activity, microstructure and morphology of low-percentage (0.05–1.0 wt%) Pt-Ru catalysts on 2%Ce/($\theta + \alpha$)-Al₂O₃ with various ratio of Pt and Ru for determination of optimum conditions of their preparation, concentration and ratio of metals, contact time, and temperature of SCOM into synthesis-gas.

2. Experimental

The Pt-Ru catalysts were prepared by the incipient wetness impregnation of the cerium-modified microspherical granules of ($\theta + \alpha$)-Al₂O₃ (granule size 100–200 μ m, specific surface area *S*_{sp} = 57.7 m²/g) with aqueous solutions of corresponding metal salts with subsequent heating on air at 873 K for 3 h. Then catalysts were reduced with a mixture of H₂:Ar = 40:60 (by volume) at raising of temperature from 623 to 1023 K with velocity 60 ml/min for 1 h. The total concentration of Pt and Ru was about 0.05%, 0.1%, 0.15%, 0.2%, 0.5%, and 1.0%. The selective catalytic oxidation of CH₄, which was present in a low concentration in a mixture of CH₄:O₂:Ar = 1.6:0.8:97.6 (vol.%), was performed in a quartz flow reactor (inner diameter of 4.5 mm) on a 0.05–1.0% Pt-Ru catalyst (a sample of 10 mg). To perform the reaction under conditions close to a plug-flow mode and to produce isothermal conditions, catalyst grains were mixed with an inert material (quartz) (particle size of 0.20–0.25 mm) in a ratio of 1:43. After reduction of samples in a H₂-Ar mixture, the system was purged by inert gas (Ar) for 0.5 h. Initial reaction mixture

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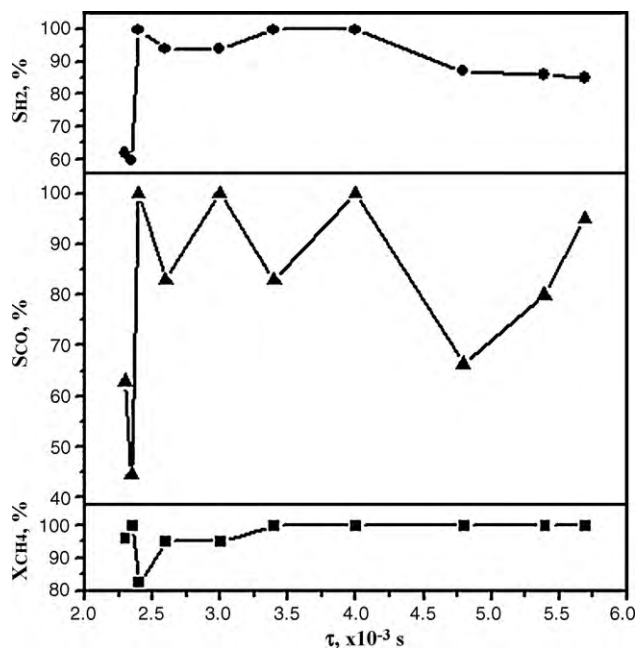


Fig. 1. Effect of contact time on selective catalytic oxidation of methane to synthesis-gas over 0.8%Pt+0.2%Ru/2%Ce/($\theta+\alpha$)-Al₂O₃ at T_{red}=1173 K, CH₄:O₂:Ar=1.6:0.8:97.6, %, CH₄:O₂=2:1, V=1.56–0.63 $\times 10^6$ h⁻¹, T=1173 K.

(CH₄/O₂/Ar=1.6/0.8/97.6 (vol.%)) was supplied into reactor with space velocity (V) 0.63–1.56 $\times 10^6$ h⁻¹. SCOM was carried out at 623–1223 K. An “Chromatec Crystall 5000.1” gas chromatograph with the software “Chromatec Analyst 2.5” equipped with a flame ionization and thermal conductivity detectors was employed for the on-line analysis of the products. Morphology, particles size, chemical composition of initial and worked out catalysts were performed on transmission electron microscope TEM-125 K with enlargement up to 120,000 times by replica method with extraction and micro diffraction. Carbonic replicas were sputtered in vacuum universal station, and carrier of catalysts was dissolved in HF. Identification of micro diffraction patterns were carried out by means of ASTM card index (1986).

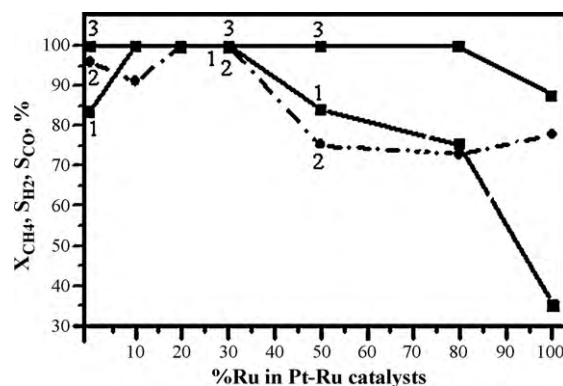


Fig. 3. Effect of the content of Ru in 1% Pt-Ru/2%Ce/($\theta+\alpha$)-Al₂O₃ catalysts on selective catalytic oxidation of methane at 1173 K, CH₄:O₂:Ar=1.6:0.8:97.6, %, CH₄:O₂=2, T=4 ms, V=0.90 $\times 10^6$ h⁻¹, T_{red}=1173 K. Data after 200 min of experiment at the general duration of 400 min are presented. 1—X_{CH₄}, 2—S_{CO}, 3—S_{H₂}.

3. Results and discussion

The effect of contact time on SCOM over 0.8%Pt-0.2%Ru/2%Ce/($\theta+\alpha$)-Al₂O₃ (V=0.63–1.56 $\times 10^6$ h⁻¹) is presented on Fig. 1. As can be seen in Fig. 1, the CH₄ conversion is varied from 82.1 up to 95.0% at contact time 2.3–2.6 ms. At contact time more than 2.6 ms the conversion increases and reaches 100% starting at $\tau=3.4$ ms (V=1.05 $\times 10^6$ h⁻¹). The maximal values (100%) of S_{H₂} were observed at 3.4–4.0 ms at simultaneous increase of S_{CO} from 95.0 up to 100%. CO₂ was not formed at $\tau=4.0$ ms (V=0.90 $\times 10^6$ h⁻¹), however reaction was performed with CO₂ formation (0.01%) at 3.0–3.4 ms. Fig. 2 shows data on SCOM to synthesis-gas over 1% Pt, Ru, and Pt-Ru on 2%Ce/($\theta+\alpha$)-Al₂O₃ with a various ratio of metals at T=1173 K, V=0.90 $\times 10^6$ h⁻¹ for 400 min. It has been determined that the CH₄ conversion decreases from 83.3 to 75.0% over 1% Pt catalyst on 100–150 min, then it raises up to 83.3–86.0% on 180 min and remains constant

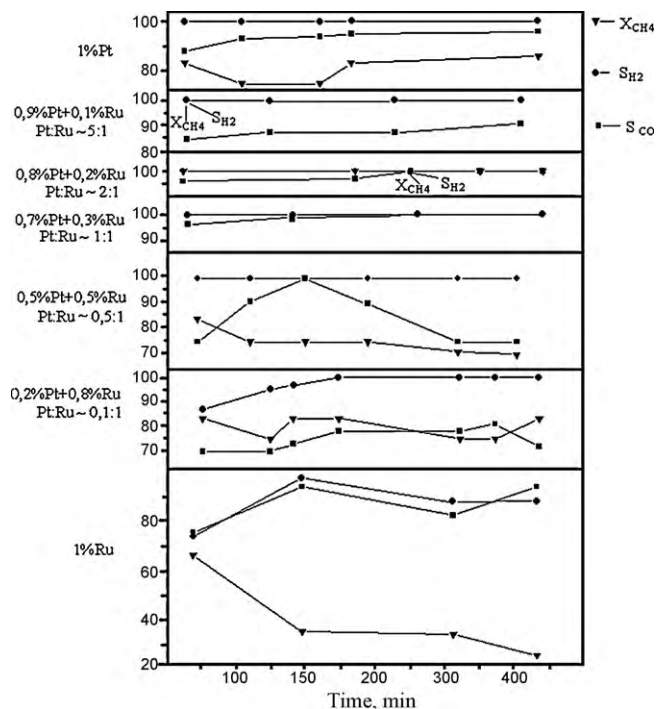


Fig. 2. Effect of Pt:Ru ratio in catalysts on conversion of methane and selectivity of product formation. CH₄:O₂:Ar=1.6:0.8:97.6, %, CH₄:O₂=2, T=4 ms, V=0.90 $\times 10^6$ h⁻¹.

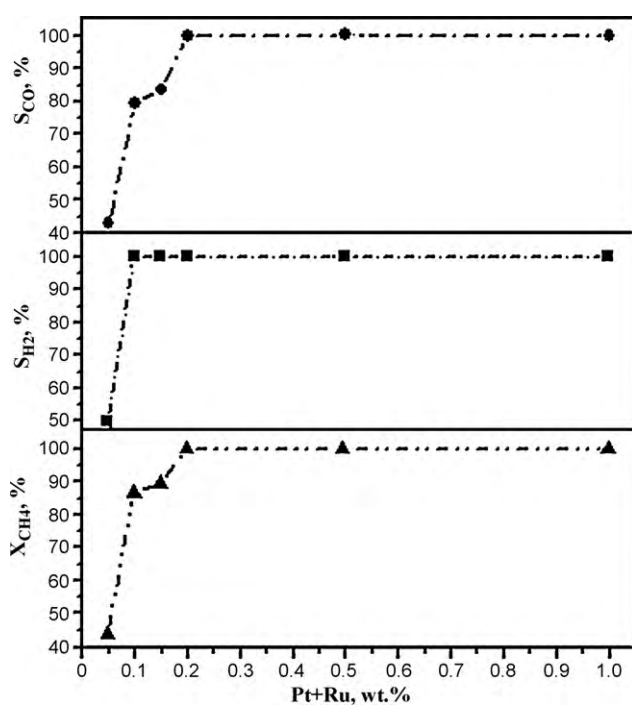


Fig. 4. Effect of concentration of the Σ Pt+Ru over 2%Ce/($\theta+\alpha$)-Al₂O₃ on selective catalytic oxidation of methane at 1173 K, T=4 ms, V=0.90 $\times 10^6$ h⁻¹, CH₄:O₂:Ar=1.6:0.8:97.6, %, CH₄:O₂=2, atomic ratio Pt:Ru ~2:1.

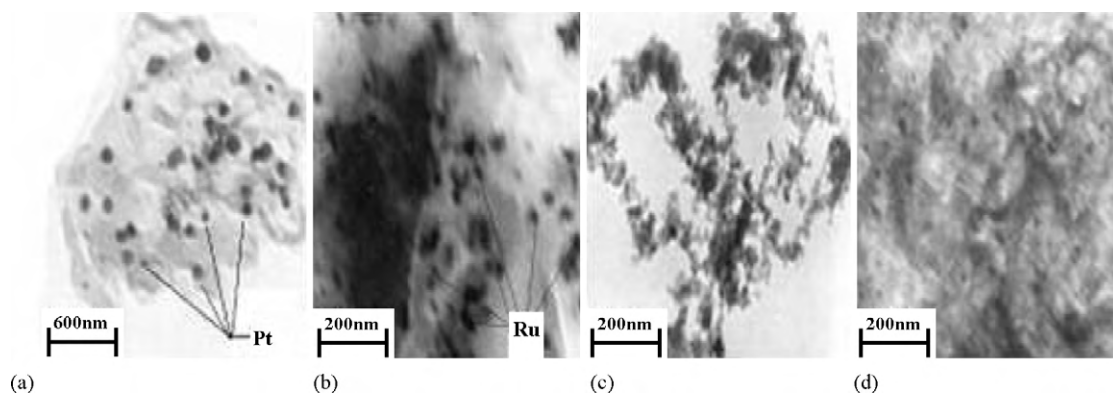


Fig. 5. Electron-microscopic photos of various phases of freshly prepared and reduced in H_2 at 573 K and 1173 K Pt-Ru/2%Ce/($\theta + \alpha$)- Al_2O_3 catalyst. a—Typical morphology of Pt^0 nano-particles, b—typical morphology of Ru^0 nano-particles, c—units of translucent particles of Ce_6O_{11} oxides, d—units of translucent particles of $CeAlO_3$ oxides.

at gradual increase of S_{CO} from 88.0 up to 96.0%. S_{H_2} did not change during all process (100%), H_2/CO ratio = 2 was established only on 400 min; CO_2 traces (0.0025%) were found in reaction products.

Introduction of 0.1 wt% Ru to 0.9 wt% Pt over 2%Ce/($\theta + \alpha$)- Al_2O_3 has led to increase of methane conversion up to 100% and S_{CO} from 84.8 to 91.0% on 120 min. H_2/CO ratio was always 2.2; there was not CO_2 in reaction products. The methane conversion, S_{CO} and S_{H_2} increased and reached the maximal 100% values on 225–230 min at the further raising of Ru content in Pt-Ru catalyst to 0.2–0.3%. The reaction performed without formation of CO_2 , H_2/CO ratio was 2 in received gas. The methane conversion decreased from 84.0 to 70.0% at maximum S_{H_2} and (0.5%Pt:0.5%Ru) content of metals. S_{CO} increased from 75.0% on 20 min up to 100% on 150 min. Then it decreased again to 75.0% on 400 min. CO_2 traces were found in reaction product, $H_2/CO = 2.2$ –2.5. S_{H_2} was 87.0% and it increased to 100% only on 175 min for 0.2%Pt-0.8%Ru catalyst. CH_4 conversion decreased from 83.3 to 75.0% and $S_{CO} = 70.0$ –73.0%. Decrease of all parameters of SCOM process was observed for 1%Ru over carrier in comparison with Pt and Pt-Ru contacts. CH_4 conversion decreased from 67.3% up to 26.8%, S_{H_2} and S_{CO} increased from 76.3 to 90.5% and from 77.7 to 96.3%, accordingly, at $H_2/CO = 2.6$ –2.9. Fig. 3 illustrates that the SCOM process proceeds worse on 1%Ru catalyst, than on Pt and Pt-Ru catalysts. It has been shown that the best results on methane conversion (curve 1), S_{H_2} (curve 3) and S_{CO} (curve 2) without CO_2 at $H_2/CO = 2$ are observed at addition of 20–30 wt% Ru to Pt and atomic Pt:Ru ratio $\sim 2:1$, or $\sim 1:1$.

Fig. 4 shows the data of SCOM to synthesis-gas at $T = 1173$ K, $V = 0.90 \times 10^6 h^{-1}$ over catalysts with various content of Pt-Ru on 2%Ce/($\theta + \alpha$)- Al_2O_3 at atomic ratio of active elements Pt:Ru $\sim 2:1$. It was shown that CH_4 conversion increases from 43.7 up to 100%, S_{CO} and S_{H_2} grow from 42.8 to 100%, and from 50.0 to 100%, accordingly, at increase of Pt + Ru content from 0.05 to 0.2 wt%. The process was performed with 100% S_{CO} and S_{H_2} at H_2/CO ratio = 2 on the catalyst with ≥ 0.2 wt% Pt + Ru.

Electron-microscopic pictures of various phases of freshly prepared Pt-Ru/2%Ce/($\theta + \alpha$)- Al_2O_3 catalyst at Pt:Ru ratio = 2:1 reduced in H_2 :Ar mixture at 573 and 1173 K are presented in Fig. 5. Typical morphology of Pt^0 and Ru^0 nano-particles (3–30 nm) are presented in Fig. 5a, b. Fig. 5c, d illustrates the units of translucent particles of Ce_6O_{11} and $CeAlO_3$ oxides (3–10 nm). Obtained data specify formation of Pt^0 , Ru^0 , Ce_6O_{11} and $CeAlO_3$ clusters. Phases of Pt-Ru alloy and $Pt_{13}Ru_{27}$ intermetallic compound were detected because there were 3 basic lines calculated on parameters of elementary cells in sets of interplane distances of the mixed phases. Probably, reaction performs due to activation and dissociation of CH_4 on Pt^0 with formation of atomic H and CH_x or C_x fragments with the subsequent recombination of atomic H to H_2 and oxidation of C_x to

CO due to surface or bulk oxygen from RuO_2 which is formed at presence of O_2 in mixture already at 573 K. Oxygen from Ce_6O_{11} is capable take part in oxidation of C_x particles up to CO, but in smaller degree because of low speed of diffusion to Pt^0 particles [3]. Besides, addition of Ce stabilizes Ru in catalysts forming perovskite-like structures and decreases the carbon deposition. The presence of Pt-Ru clusters with Pt:Ru = 2:1, 1:1 considerably facilitates interaction of CH_4 with O_2 because of possible separate adsorption and activation of components on different parts of cluster: CH_4 —on Pt^0 , and O_2 —on Ru^0 .

Thermal desorption of H_2 has demonstrated that there are 4 areas of allocation of molecular and atomic forms of H_2 adsorption at different temperatures. Pt and Pt-Ru contacts are capable to adsorb on a surface more quantity of firmly combined hydrogen, than catalyst with $>0.5\%$ Ru. It has been found that SCOM parameters (X_{CH_4} , S_{CO} , S_{H_2}) correlate with part of firmly combined H_{ads} at decrease the content of metals. It is demonstrated that both X_{CH_4} , S_{H_2} , S_{CO} , and part of H_{ads} are increased according to growth of Pt + Ru content from 0.05 to 0.2%.

4. Conclusion

Optimum conditions ($\tau = 4$ ms, $T = 1173$ K, $CH_4:O_2 = 2:1$ in argon) for production of synthesis-gas with H_2/CO ratio = 2 without CO_2 formation were determined during comparative research of low-percentage Pt, Ru and Pt-Ru catalysts supported on 2%Ce/($\theta + \alpha$)- Al_2O_3 in SCOM reaction. That ratio is optimal for Fischer-Tropsch synthesis of methanol and hydrocarbons. It was found that Pt-Ru catalyst containing ≥ 0.2 wt% of the sum of metals at atomic ratio Pt:Ru $\sim 2:1$, or $\sim 1:1$ are the most active ($X_{CH_4} = 100\%$) and selective ($S_{CO,H_2} = 100\%$). It was shown by TEM method that particles of Pt^0 (7.5–15.0 nm), Ru^0 (5.0–30.0 nm), Ce_6O_{11} (3.0–10.0 nm), $CeAlO_3$ (3.0–5.0 nm), and also Pt-Ru alloy in the mixed catalysts and intermetallic compounds of $Pt_{13}Ru_{27}$ ($3.0 \leq d \leq 18.0$) with a simple cubic lattice are formed at reduction of catalysts in H_2 -Ar mixture at 573–1173 K. Presence of the above-stated particles on a surface of the catalyst promotes selective production of synthesis-gas.

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