

Thus, the optimal conditions of deep oxidation of toluene on oxide Ni-, Cu- and Cr-containing catalysts over 2% Ce/ θ -Al₂O₃ were determined. Degree of conversion of toluene reaches 98.5 – 98.8% on the Ni-Cu-Cr/2% Ce/ θ -Al₂O₃ catalyst at temperatures of 723 - 773 K, GHSV - 5410³ h⁻¹ and the concentration of toluene in the initial mixture with air – 100 - 320 mg m⁻³.

The intensive reflections from CuO and less intensive from NiO, CeO₂, and θ -Al₂O₃ are observed in roentgenograms of the Ni-Cu-Cr/2% Ce/ θ -Al₂O₃ catalyst heated at 873 K. Not only CeO₂ crystallization, but a sharp increase in the content of α -Al₂O₃ starting from 1,273 K is a result of heating of the Ni-Cu-Cr/2% Ce/ θ -Al₂O₃ catalyst. Significant reduction of the total surface area of catalysts is due to heating. CeO₂ crystallization occurs to a lesser extent due to the small (2%) of Ce content (in carrier only). According to XRD the presence of CeO₂ crystals and X-ray amorphous clusters with diameters from 20 to 100 E, metal oxides of variable valence NiO, CuO, and solid solutions of metals CuO (NiO) is fixed on the surface of carrier in the process of catalyst synthesis after heating at 873 K. Phase transformations occur in the Ni-Cu-Cr catalyst upon heating in air above 1,273 K. Metal oxides react with alumina to form the Me-Al₂O₄ type aluminates with diameter from 200 to 1,000 E and the surface decreases sharply to 2 - 5 m². Reflexes from the θ -Al₂O₃, α -Al₂O₃, and CeO₂ are presented in the 2% Ce/ θ -Al₂O₃, as well as in the carrier (quantification was performed by reflections 2.31 E, 1.74 E, 1.91 E, respectively). The intensity of CeO₂ reflexes increases slightly with increasing the Ce content in catalyst, and especially after the heating consistently at 873, 1,073, 1,273, 1,373 and 1,473 K. This indicates that crystallization of the amorphous cerium oxides happens as a result of heating. The same process is characteristic for supported on the 2% Ce/ θ -Al₂O₃ catalysts, but to different degrees.

Thus, the use of X-ray diffraction analysis to study of polyoxide catalysts supported on 2% Ce/ θ -Al₂O₃ showed that the active components are mainly in amorphous state in the initial catalysts; part of Ni and Cu is represented by Ni and Cu oxides [17].

The morphology and particle size of the developed catalysts were examined by transmission electron microscope on the EM-125K at magnification 80,000 times by the replica method with extraction using electron microdiffraction. It was found that single, double and triple metal oxides, the particle size of which are decreased from 50-80 E (Ce/Al₂O₃) to 20-30 E (Ni-Cu-Cr) are formed at complication the composition of three-component catalyst. The nanoparticles of metal oxides or their mixtures are formed after decomposition of nitrates of initial oxide Ni-Cu-Cr catalyst at 873 K according to electron microscopy and microdiffraction. Interaction of elements with θ -Al₂O₃ carrier with formation of larger copper and nickel aluminates of the AB₂O₄ and ABO₃ type occurs when the temperature rises [18].

Figure 1 shows the spectra of thermal desorption of oxygen from the oxide Ni-Cu-Cr/ θ -Al₂O₃ after oxygen adsorption at 873 K. It is seen that the amount of oxygen released upon heating to 1,173 K (stabilizing temperature) increases with the complexity of the composition of mixed catalyst. Desorption curve has bends at 773 K and 923 K as well as maximum at 1,023 K, which is caused by desorption of the adsorbed oxygen (673 – 873 K) and decomposition (873-1,073 K) of copper and nickel oxides (up to Cu₂O, Ni₂O) and then mixed oxides (> 1,070 K).

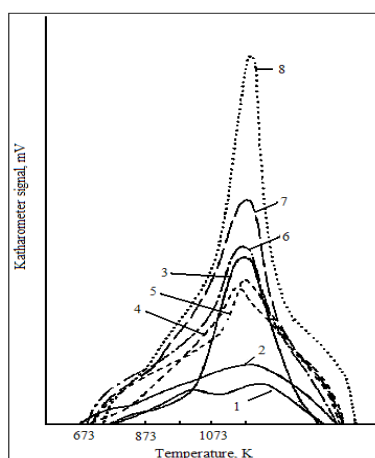


Figure 1 – Thermal desorption of oxygen from the catalysts on Al₂O₃ after heating in air:
 1-5% Ni, 2-5% Cu, 3-5% Cr, 4-5% (Ni + Cr), 5-5% (Cu + Cr), 6-8-10% Ni-Cu-Cr at varying the deposition methods of catalysts:
 6 - NH₄HCO₃, 7 - Al(NO₃)₃, 8 - NH₄HCO₃ + Al(NO₃)₃, T – 873 K, 1 h