

Application of Oxide Copper Chromium Catalysts for the Purification of Exhaust Gases

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Results of the development of multicomponent oxide catalysts based on Ni, Cu, and Cr supported on 2 % Ce/ θ -Al₂O₃ by varying the concentration of the active phase of catalyst are presented in paper. It was found that the highest degree of toluene conversion (up to 98.8 %) is observed on the three- component Ni-Cu-Cr/2 % Ce/ θ -Al₂O₃ catalyst with optimal metal ratio Ni : Cu : Cr = 1.0 : 3.0 : 0.1 at GHSV = 5×10^3 h⁻¹ and a temperature of 723 - 773 K. The presence of CeO₂ crystals, X-ray amorphous clusters ($d = 20 - 100$ Å) of variable valence metal oxides NiO and CuO as well as solid metal solutions CuO (NiO) was detected on the surface of optimum catalyst calcined at 873 K using XRD and electron microscopy methods.

1. Introduction

The problem of chemical safety and sanitary air protection is particularly relevant due to the increase of harmful emissions of industrial enterprises, which have a strong toxic effect. Harmful emissions of the industrial enterprises (paint, furniture, cable, pharmaceutical, printing) and transport are the main pollutants of cities. Many chemical compounds (toluene, xylene, styrene, phenol, tricresol, mineral spirits, CO, etc.), which negatively affect the living organism and flora are harmful toxic emissions from industrial plants. Under the Kyoto agreement, adopted in December 1997, in addition to the United Nations Framework Convention on Climate Change (UNFCCC), developed countries and countries with economies in transition have to reduce or stabilize greenhouse gas emissions (Nikolaev, 2008). Large volumes of industrial emissions occur mainly in large cities, where their maximum permissible concentration (MPC) is much higher than the norm. The content of harmful emissions above the MPC in industrial workshops and atmospheric air in the cities cause a negative impact on living organisms and lead to various diseases thereby creates a threat to the safety of the environment (Jecha et al., 2013). Toluene, xylene and ethyl-benzene are major part of the solvents used in various industries, which are present in gaseous emissions (Brattoli et al., 2014). Toxic and adverse effect of harmful emissions on a living organism can be traced on the example of toluene - a major component of toxic organic gaseous emissions that are present in the emissions of furniture, paint, cable, printing and other industries. For example, the toluene content, which is above the threshold concentration in manufacturing plants causes a headache, dizziness, infringement of taste and smell, irritation of eyes, nose and throat. The inhalation of toluene with a concentration of 250 mg/m³ for 2 h leads to a decrease in heart rate, disturbance of speech, movement coordination (Zheksenbaeva et al., 2012). Prolonged inhalation of toluene, which is present in the composition of glue, varnishes, paints, etc., causes neurotoxic deviations that lead to clinical consequences - hallucinations, somnolence, suicide attempts, visual disturbances and seizures. In some cases, prolonged inhalation leads to hypoglycaemic paralysis.

From the literature data (Popova et al., 2006) on the methods and apparatuses for neutralization of toxic emissions follows that deep catalytic oxidation is the most economical way for cleaning of gases from the emissions of complex composition. Typically, the catalysts based on noble metals (Pt, Pd) (Tidahy et al.,

2007), which have high activity (95 – 100 %) in complete oxidation of organic substances (Kim et al., 2013), are used mainly for cleaning of waste gas of industrial enterprises. Catalysts based on platinum group metals have high activity at low temperatures, durability, heat resistance and ability to operate stably at high space velocities. Conditions of deficit and high cost of platinum group metals lead to the need to develop new approaches to the creation of highly effective polyoxide catalysts that do not contain noble metals capable exhibit a high thermal stability and poison-resistance and sustainable in the long term operation (Tungatarova et al., 2014). Creation of catalysts for gas purification, which do not contain noble metals or contain them in small amounts, is an important goal. The use of low-percentage catalysts based on transition metals and their oxides on carriers is one of the most promising ways to solve this problem. In this context, the development of high-performance polyoxide catalysts, which do not contain precious metals, and technology for deep oxidation of toxic organic gaseous emissions from industry are relevant for the Republic of Kazakhstan. Preparation of polyoxide supported catalysts with desired properties, as well as study the influence of catalyst composition and modified additives on deep oxidation of toluene - a major component of toxic organic gaseous industry emissions to CO₂ and H₂O, is the goal of research.

2. Experimental

Polyoxide catalysts were prepared by capillary impregnation of alumina modified with cerium by mixed aqueous solutions of metal nitrates by incipient wetness of carrier with subsequent drying under 453 – 473 K (4 – 5 h) and calcination at 873 K (1 – 1.5 h) in air. Deep oxidation of toluene was carried out on the PKU-2VD catalytic installation intended for testing of catalysts at pressures up to 3.4 MPa. Analysis of the initial mixture and reaction products were carried out using CHROMOS GC-1000 chromatograph with CHROMOS software. The temperature of thermal conductivity detector – 473 K, evaporator temperature – 553 K, column temperature - 313 K. The rate of carrier gas Ar - 10 ml/min. Catalytic activity of catalysts was determined in flow installation at deep oxidation of toluene in air at various temperatures (523 – 773 K), space velocities (5 - 15×10³ h⁻¹) and toluene concentration (320 mg/m³) in the initial mixture. The phase composition of catalysts was determined by X-ray diffractometer DRON-4.7, Co anode, 25 kV, 25 mA, 2θ – 5 - 80° (XRD). The BET specific surface area was determined by adsorption method using an Accusorb instrument (Micromeritics, United States) at the low temperature adsorption of N₂. The morphology, particle size, chemical composition of the Ni-Cu-Cr catalysts were investigated by transmission electron microscope EM-125K at 80,000 magnification by the replica method with extraction using a microdiffraction.

3. Results and Discussion

3.1 Catalytic results

Results on study of activity of polyoxide catalysts in the reaction of deep oxidation of toluene at 723 K and space velocity 5 × 10³ h⁻¹ are shown in Figure 1. As seen in Figure 1, the conversion of toluene increased with the complexity of the composition of catalysts. The lowest degree of toluene oxidation (57.0 %) was observed on the 5 % Ni/2 % Ce/θ-Al₂O₃ catalyst, and the greatest degree (up to 98.5 %) was observed on the three-component 9 % NiCuCr/2 % Ce/θ-Al₂O₃ catalyst. From the obtained experimental data the developed catalysts may be disposed in following series by activity in the reaction of deep oxidation of toluene: NiCuCr/2 % Ce/θ-Al₂O₃ (98.5 %) > NiCuCr/θ-Al₂O₃ (92.0 %) > NiCu/2 % Ce/θ-Al₂O₃ (84.0 %) > NiCr/2 % Ce/θ-Al₂O₃ (75.0 %) > Ni/2 % Ce/θ-Al₂O₃ (57.0 %). The degree of conversion of the initial toluene into carbon dioxide on the NiCu/2 % Ce/θ-Al₂O₃, NiCr/2 % Ce/θ-Al₂O₃ and CuCr/2 % Ce/θ-Al₂O₃ catalysts were 84.0, 74.0 and 67.0 %, respectively. Analysis of experimental data shows that the largest conversion of toluene is observed on three-component NiCuCr/2 % Ce/θ-Al₂O₃ catalyst with an optimal ratio of metals Ni : Cu : Cr = 1.0 : 3.0 : 0.1 at T = 723 K. Effect of process parameters (temperature, space velocity, concentration of toluene in gaseous mixture) on the completeness conversion of toluene (to CO₂ and H₂O) on the NiCuCr/2 % Ce/θ-Al₂O₃ polyoxide catalyst was studied. The degree of toluene oxidation from the variation of space velocities at different temperatures on the NiCuCr/2 % Ce/θ-Al₂O₃ catalyst are presented in Table 1. It can be seen that with the increase of space velocity from 5×10³ to 15×10³ h⁻¹ the degree of toluene oxidation reduces from 98.5 to 89.3 %, respectively.

Thus, degree of conversion of toluene to CO₂ reaches the 98.5 – 98.8 % on the NiCuCr/2 % Ce/θ-Al₂O₃ catalyst at a temperature of 723 – 773 K and space velocity 5×10³ h⁻¹.

Influence of concentration of toluene in the initial mixture to the efficiency of its conversion on the polyoxide catalysts of various compositions were studied. Table 2 shows that increasing the concentration of toluene from 100 to 320 mg/m³ in the initial mixture with air leads to a slight decrease in the degree of conversion of toluene on the two component NiCu/2 % Ce/θ-Al₂O₃ and CuCr/2 % Ce/θ-Al₂O₃ catalysts. A noticeable decrease in activity among two component oxide catalysts were found on the nickel-chromium-containing catalyst from 76.6 to 73.0 %. NiCuCr/2 % Cr/θ-Al₂O₃ catalyst was the most stable.

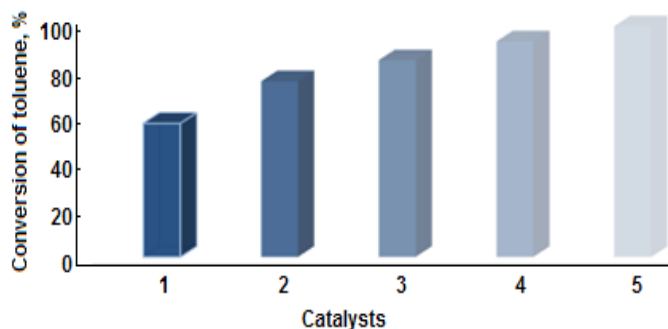


Figure 1: The oxidation of toluene on the oxide NiCuCr catalysts at 723 K and GHSV $5 \times 10^3 \text{ h}^{-1}$: 1 – 5 % Ni/2 % Ce/ θ -Al₂O₃, 2 – 5 % NiCu/2 % Ce/ θ -Al₂O₃, 3 – 5 % NiCr/2 % Ce/ θ -Al₂O₃, 4 – 5 % CuCr/2 % Ce/ θ -Al₂O₃, 5 – 9 % NiCuCr/2 % Ce/ θ -Al₂O₃

Table 1: Effect of temperature and space velocity on the degree of conversion of toluene on the NiCuCr/2 % Ce/ θ -Al₂O₃ catalyst

T, K	Space velocity, $\times 10^3 \text{ h}^{-1}$		
	5	10	15
Degree of toluene conversion, %			
523	73.7	81.0	82.1
573	89.5	85.7	83.8
623	94.7	90.5	85.7
673	97.5	91.5	89.3
723	98.5	93.5	89.3
773	98.8	95.2	89.3

Note: The concentration of toluene in the feed - 320 mg/m³

Table 2: Effect the content of toluene in the initial mixture with air on degree of its conversion on the various catalysts

Catalysts	Concentration of toluene, mg/m ³	
	100	320
Degree of conversion of toluene, %		
5 % CuCr/2 % Ce/ θ -Al ₂ O ₃	68.0	67.9
5 % NiCr/2 % Ce/ θ -Al ₂ O ₃	76.6	73.0
5 % NiCu/2 % Ce/ θ -Al ₂ O ₃	85.0	84.0
9 % NiCuCr/2 % Ce/ θ -Al ₂ O ₃	98.5	98.8

Note: T – 723 K; GHSV - $5 \times 10^3 \text{ h}^{-1}$

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 NiCuCr/2 % Ce/ θ -Al₂O₃ catalyst at temperatures of 723 – 773 K, GHSV - $5 \times 10^3 \text{ h}^{-1}$ and the concentration of toluene in the initial mixture with air – 100 - 320 mg/m³.

Deep oxidation of toluene on NiCuCr/2 % Ce/ θ -Al₂O₃ catalyst promoted with small additions (0.05 %) of palladium and platinum at various temperatures and space velocities was also studied. The dependence of toluene conversion from temperature on catalysts at GHSV - $5 \times 10^3 \text{ h}^{-1}$ and toluene concentration = 320 mg/m³ shown in Figure 2. It was found that the conversion of toluene increases as the temperature rises and reaches 99.0 % at 723 K on polyoxide NiCuCr/2 % Ce/ θ -Al₂O₃ catalyst promoted with palladium. A further increase in the reaction temperature to 773 K does not change the activity of catalyst. The same dependence of activity from temperature was established for catalyst promoted with platinum. The conversion of toluene on the Pt-containing catalyst is higher than on the polyoxide and Pd-containing catalysts and reaches 100 %. In addition, a high degree of toluene conversion at temperature, which is lower by 50 K than that for other samples, is observed on NiCuCr + Pt/2 % Ce/ θ -Al₂O₃ sample, unlike the three-component catalyst and the sample promoted by Pd.

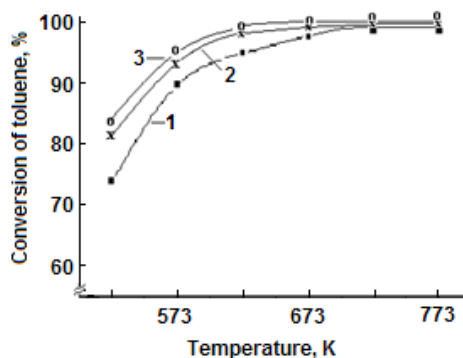


Figure 2: Dependence of the degree of toluene oxidation from temperature and composition of catalysts at GHSV - $5 \times 10^3 \text{ h}^{-1}$ and toluene concentration = 320 mg/m^3 : 1 - NiCuCr/2 % Ce/ θ -Al₂O₃, 2 - NiCuCr+Pd/2 % Ce/ θ -Al₂O₃, 3 - NiCuCr+Pt/2 % Ce/ θ -Al₂O₃

A study on the effect of space velocity on conversion of toluene has shown (Figure 3), that the maximum degree of toluene conversion is reached at $5 \times 10^3 \text{ h}^{-1}$ on all catalysts. Increase the space velocity more than $5 \times 10^3 \text{ h}^{-1}$ leads to a gradual reduction of catalytic activity of developed systems. Thus, the Pd-containing catalyst maintains its activity up to $10 \times 10^3 \text{ h}^{-1}$ and then decrease of catalyst activity is observed. Pt-containing catalyst on which degree of toluene conversion (100 %) is not reduced at space velocity up to $15 \times 10^3 \text{ h}^{-1}$ is the most active. Promoted catalysts are arranged in series on activity in the reaction of deep conversion of toluene: NiCuCr/2 % Ce/ θ -Al₂O₃ < NiCuCr + Pd/2 % Ce/ θ -Al₂O₃ < NiCuCr + Pt/2 % Ce/ θ -Al₂O₃. Thus, the promotion by small additions of Pd and Pt (0.05 %) increases the activity of synthesized polyoxide three-component NiCuCr/2 % Ce/ θ -Al₂O₃ catalyst in the reaction of deep conversion of toluene.

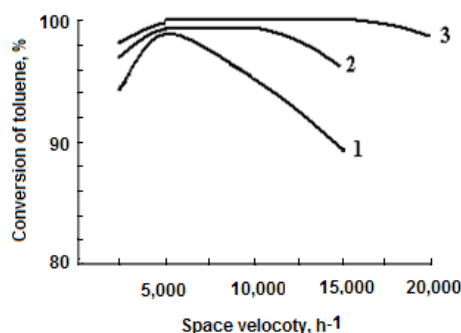


Figure 3: Effect of space velocity on conversion of toluene at the toluene concentration of 320 mg/m^3 in the initial mixture: 1 - NiCuCr/2 % Ce/ θ -Al₂O₃, 2 - NiCuCr + Pd/2 % Ce/ θ -Al₂O₃, 3 - NiCuCr + Pt/2 % Ce/ θ -Al₂O₃

3.2 The study of polyoxide catalysts based on Ni-, Cu-, Cr- on 2 % Ce/ θ -Al₂O₃ by X-ray diffraction analysis

The intensive reflections from CuO and less intensive from NiO, CeO₂, and θ -Al₂O₃ are observed in roentgenograms of the NiCuCr/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 NiCuCr/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 Å, 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 NiCuCr 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 Å and the surface decreases sharply to 2 – 5 m². The results of the phase composition of catalysts after heating at 873 K for 1 h are shown in Figures 4 and 5. Reflexes from the θ -Al₂O₃, α -Al₂O₃, and CeO₂ are present in the 2 % Ce/ θ -Al₂O₃, as well as in the carrier (quantification was performed by reflections 2.31 Å, 1.74 Å, 1.91 Å, respectively). The intensity of CeO₂ reflexes increases slightly with increasing the cerium 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 oxide happens as a result of heating. The same process is characteristic for supported on the 2 % Ce/ θ -Al₂O₃ catalysts, but to different degrees.

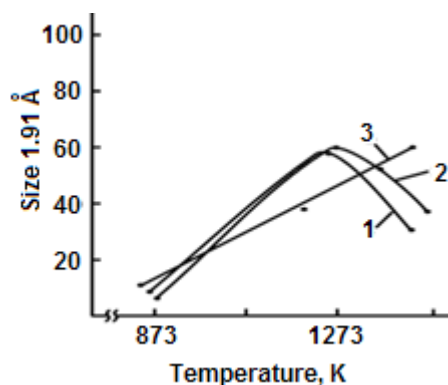


Figure 4: Dependence of the intensity of CeO₂ reflection (1.91 Å) from the heating temperature: 1 - Ni₁Cu₃Cr_{0.1}, 2 - Ni₁Cu₃Cr_{0.1} + Pt, 3 - Ni₁Cu₃Cr_{0.1} + Pd

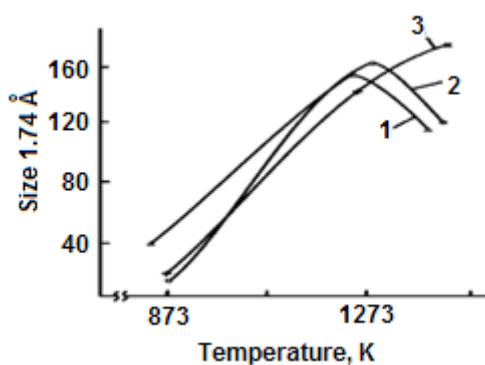


Figure 5: Effect of the heating temperature on relative content of the α -Al₂O₃ (1.74 Å) in polyoxide NiCuCr/2 % Ce/ θ -Al₂O₃ catalyst: 1 - Ni₁Cu₃Cr_{0.1}, 2 - Ni₁Cu₃Cr_{0.1} + Pt, 3 - Ni₁Cu₃Cr_{0.1} + Pd

Promotion of NiCuCr catalyst with Pd and Pt also contributes to phase transformations in catalyst under heating. Weak reflexes from NiO, Ce₆O₁₁ and NiAl₁₀O₁₆ are available in roentgenogram in addition to the formation of crystalline CeO₂, α -Al₂O₃, CuO and Ni(Cu)Al₂O₄.

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, especially at the promotion by Pt in NiCuCr catalyst.

3.3 The study of multicomponent oxide catalysts based on NiCuCr over 2 % Ce/ θ -Al₂O₃ by electron microscopy

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 (Figure 6). It was found that single, double and triple metal oxides, the particle size of which are decreased from 50 - 80 Å (Ce/Al₂O₃) to 20 - 30 Å (NiCuCr) are formed at complication the composition of three-component catalyst.

Two types of particles: fine oxides (60 - 150 Å) and larger aluminates are formed at introduction of Pt and Pd into NiCuCr catalyst. Particles with size of more than 1,000 Å are found at promotion by Pd, especially during heating up to 1,473 K. Most of the particles are finely dispersed which become larger to 200 - 500 Å after heating at 1,473 K due to formation of aluminates and chromates at promotion by Pt. Relative content of the large particles of aluminates in the NiCuCr catalyst increases at promotion by Pt and Pd and after high-temperature heating. The nanoparticles of metal oxides or their mixtures are formed after decomposition of nitrates of initial oxide NiCuCr 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 (Komashko et al., 2002).

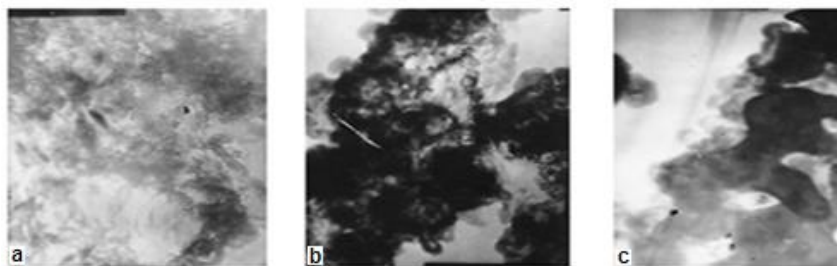


Figure 6: TEM images of the supported three-component catalyst: a – NiCuCr (873 K), b – NiCuCr + Pd (873 K), c – NiCuCr + Pd (1,473 K)

4. Conclusions

As a result of studies, it was found that the highest degree of toluene conversion (to 98.8 %) is observed on three-component NiCuCr/2 % Ce/ θ -Al₂O₃ catalyst with optimal ratio Ni : Cu : Cr = 1.0 : 3.0 : 0.1 at space velocity of $5 \times 10^3 \text{ h}^{-1}$ and temperature 723 - 773 K. It was determined that the promotion by small (0.05 %) Pt and Pd additives of the synthesized NiCuCr/2 % Ce/ θ -Al₂O₃ catalyst increase the conversion of toluene to CO₂ and water to 100 %. The presence of CeO₂ crystals and X-ray amorphous clusters ($d = 20 - 100 \text{ \AA}$) of metallic NiO, CuO oxides of variable valence and solid solutions CuO (NiO) was detected on the surface of NiCuCr catalyst calcined at 873 K by X-ray diffraction analysis and electron microscopy. Phase transformations occur in NiCuCr catalyst upon heating in air above 1,273 K. The metal oxides react with alumina to form MeAl₂O₄ type aluminate with $d = 200 - 1,000 \text{ \AA}$ with simultaneous decrease of specific surface area.

Acknowledgments

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