

Oxide Ni-Cu Catalysts for the Purification of Exhaust Gases

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Currently, special attention is paid to the environmental friendliness of modern chemical industries. Significant volumes of volatile organic compounds are released into the air annually and harm the environment as well as human health. Industrial waste gas treatment is an important component in environmental protection. The catalytic purification of toxic compounds occupies a special place in minimizing the generated waste. Compositions based on noble metals, especially platinum, palladium and ruthenium, which are very expensive, are the best catalysts. The aim of this work is to create catalysts for the purification of gases that do not contain noble metals. The results of the development of low-cost selective multicomponent oxide catalysts based on Ni, Cu, and Cr supported on 2 % Ce/θ - Al₂O₃ for the purification of volatile organic compounds using toluene as an example are presented in the paper. It was found that the highest degree of toluene conversion (up to 98.8 %) is observed on a three-component Ni - Cu - Cr/2 % Ce/θ - Al₂O₃ catalyst with an optimal ratio of metals Ni : Cu : Cr = 1.0 : 3.0 : 0.1 at a temperature of 723 - 773 K.

1. Introduction

Chemical safety and sanitary protection of the air are very relevant in connection with the increase in harmful emissions of industrial enterprises, which have a strong toxic effect on the environment. Most chemical compounds (toluene, xylene, styrene, phenol, tricresol, mineral alcohols, CO), which adversely affect on living organisms and flora, are harmful toxic emissions from industrial enterprises. Developed countries and countries with economies in transition have to reduce or stabilize greenhouse gas emissions under the Paris agreement, adopted on December 12, 2015 and signed on April 22, 2016, in addition to the United Nations Framework Convention on Climate Change (UNFCCC) (Reckien et al., 2018). The content of harmful emissions above the maximum permissible concentration in industrial plants and atmospheric air in cities has a negative effect on living organisms, which leads to various diseases. It poses a threat to environmental safety (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 organisms 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 inhalation of toluene with a concentration of 250 mg m⁻³ for 2 h leads to a decrease in heart rate, speech impairment, and movement coordination (Zheksenbaeva et al., 2012). Prolonged inhalation of toluene, which is present in the composition of glue, varnishes, paints, causes neurotoxic deviations that lead to clinical consequences - hallucinations, somnolence, suicide attempts, visual disturbances and seizures.

Deep catalytic oxidation is the most economical method for cleaning of gases from the emissions of complex composition (Duplančić et al., 2017), which follow from the literature data (Popova et al., 2006) on the methods and apparatuses for neutralization of toxic emissions. 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 (Tong et al., 2019). Catalysts based on platinum group metals have high activity at low temperatures, durability, heat resistance and ability

to operate stably at high space velocities. The high cost of the platinum group metals is the reason for the development of new approaches to the creation of highly efficient polyoxide catalysts that do not contain noble metals, and which are able to exhibit high thermal stability and resistance to poisoning over a long period of operation (Tungatarova et al., 2014). Creation of catalysts for gas purification, which do not contain noble metals or contain them in small amounts (Zhang et al., 2019), is an important goal. The development of high-performance polyoxide catalysts, which do not contain noble metals and technology for deep oxidation of toxic organic gaseous emissions from industry are relevant. The creation of clean production without harmful exhaust gases and volatile impurities is important today. To achieve these goals, Ni - Cu - Cr catalysts were studied for the purification of volatile organic compounds using toluene by a set of physico-chemical methods to determine the state of active components on the catalyst surface, to increase the activity and stability of samples at high temperatures.

2. Experimental

The Ni - Cu - Cr/2 % Ce/ θ - Al_2O_3 catalyst was investigated by the temperature-programmed desorption (TPD) of oxygen and temperature-programmed reduction (TPR) of hydrogen. The adsorption characteristics of the developed catalyst were investigated on the "Chemosorb" analyzer designed for automated TPR and TPD analysis. The oxidized catalyst is heated by a program-controlled process in TPR method. Reducing gas (hydrogen) is passed through it at the same time. The TPD method was used to study pre-activated samples that were saturated with the test reaction gas (oxygen) under isothermal conditions after preparation. The sample was heated at a constant rate and purged with an inert gas (argon) during analysis. The gas that was initially chemisorbed on the surface of the sample began to desorb. The concentration of gas desorbed from the sample was recorded using a thermal conductivity detector.

3. Results and Discussion

Figure 1 shows the spectra of thermal desorption of oxygen from oxide Ni - Cu - Cr/ θ - Al_2O_3 catalysts after adsorption of oxygen at 870 K. It can be seen that the amount of oxygen released upon heating to 1,173 K (stabilizing temperature) is increased as the complexity of the composition of the mixed catalyst.

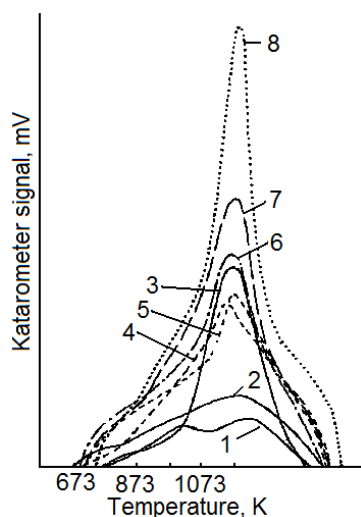


Figure 1: O_2 - TPD profiles of the catalysts on Al_2O_3 after heating in air: 1 - 5 % Ni, 2 - 5 % Cu, 3 - 5 % Cr, 4 - 5 % (Ni + Cr), 5 - 5 % (Cu + Cr), 6 - 8 - 10 % Ni - Cu - Cr at varying the supporting methods of catalysts: 6 - NH_4HCO_3 , 7 - $\text{Al}(\text{NO}_3)_3$, 8 - $\text{NH}_4\text{HCO}_3 + \text{Al}(\text{NO}_3)_3$, $T = 873$ K, 1 h

The desorption curve has kinks at 773 K, 923 K and a maximum at 1,023 K, which is due to the desorption of adsorbed oxygen (673 - 873 K) and the decomposition at first (873 - 1,073 K) of copper and nickel oxides (to Cu_2O , Ni_2O), and then mixed oxides ($> 1,070$ K). The total amount of released oxygen (9.7 mmol per 1 g of active phase) exceeds the possible sorption in each of the oxides. This is obviously due to the dissolution of oxides in the resulting solid solutions in excess of stoichiometric oxygen released at lower temperatures. The total amount of oxygen released from the Ni - Cu - Cr catalyst (mainly due to the weakly adsorbed oxygen)

depends on the conditions for obtaining of mixed carbonates and their decomposition. It is increased by 2 times when using $\text{NH}_4\text{HCO}_3 + \text{Al}(\text{NO}_3)_3$ in the precipitation mixture.

Calculation of the activation energy of oxygen evolution from the catalyst showed that it is 88 - 89 kJ mol^{-1} for adsorbed oxygen. Desorption energy (E_{des}) for single copper oxides is equal to 128 kJ mol^{-1} , for nickel oxides - 120 kJ mol^{-1} , and for mixed oxides - 140 - 144 kJ mol^{-1} .

The thermal desorption spectra of oxygen from Ni - Cu - Cr catalysts on 2 % Ce/ θ - Al_2O_3 correspond to those described above for the catalyst supported on θ - Al_2O_3 . Calculation of the amounts of released oxygen indicates a significant decrease in specific sorption to 0.64 mmol g^{-1} of the active phase.

Increase in specific adsorption is facilitated by the introduction of Pt (0.93 mol g^{-1}) and Pd (0.75 mmol g^{-1}) into the composition of catalyst. The promoters cause a decrease in the decomposition temperature of mixed oxides by ~ 100 K. The activation energy of desorption differs little from those found for Ni - Cu - Cr supported on θ - Al_2O_3 : E_{des} adsorbed is 90.8 and reaches 96 - 98 kJ mol^{-1} on promoted contacts. E_{des} at the decomposition of mixed oxides is 142 kJ mol^{-1} .

The heating of Ni - Cu - Cr/2 % Ce/ θ - Al_2O_3 at 1,473 K (Figure 2) sharply reduces the release of oxygen in the region of decomposition of metal oxides for the initial and promoted contacts. The adsorbed oxygen region completely disappears in the spectrum of Ni - Cu - Cr and Ni - Cu - Cr + Pt catalysts. The observed phenomena can be explained by the fact that most of the metal oxides interact with the carrier with the formation of large (20 - 100 nm) Ni(Cu) Al_2O_4 aluminates (as shown by the X-ray diffraction method (XRD) and transmission electron microscopy (TEM) methods with microdiffraction). The total surface of the catalysts decreases from 60 to 5 $\text{m}^2 \text{g}^{-1}$, although the content of active elements in the catalyst did not change significantly during heating (emission spectral analysis) (Table 1).

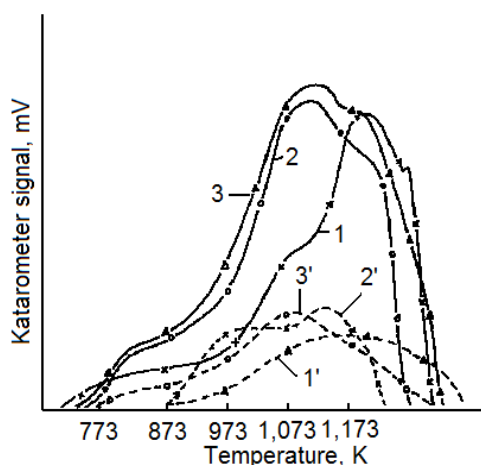


Figure 2: O_2 - TPD profiles of the Ni - Cu - Cr/2 % Ce/ Al_2O_3 catalyst heated in oxygen and promoted with Pd and Pt: 1 - Ni - Cu - Cr/2 % Ce/ Al_2O_3 , 2 - Ni - Cu - Cr/2 % Ce/ Al_2O_3 + Pd, 3 - Ni - Cu - Cr/2 % Ce/ Al_2O_3 + Pt. 1', 2', 3' - catalysts after heating at 1,473 K, T - 873 K

Table 1: Content of elements in the catalysts according to the data of the method of emission-spectral analysis after heating at different temperatures

Catalysts	T, K	Content of elements, %		
		Ni	Cu	Cr
Ni - Cu - Cr/2 % Ce/ θ - Al_2O_3	873	1.8	3.3	0.12
Ni - Cu - Cr/2 % Ce/ θ - Al_2O_3	1,373	1.6	3.1	0.15

The study of the temperature-programmed reduction of Ni - Cu - Cr catalysts on 2 % Ce/ θ - Al_2O_3 made it possible to better understand the mechanisms of oxygen reduction and oxygen removal processes, and also to evaluate the ability of catalysts to adsorb oxygen from the gas phase.

Figure 3a shows that the TPR curve has 4 temperature absorption maxima of H_2 : $T_1 = 523$ K, $T_2 = 573$ K, $T_3 = 673$ K and $T_4 = 1,073$ K, corresponding to the reduction of CuO (T_1), mixed oxides of CuO - NiO (T_2), NiO (T_3) and partially formed Ni or Cu aluminates. The temperature-programmed oxidation (TPO) of the catalyst after its reduction to 1,225 K (Figure 3b) showed that in contact oxygen is readily adsorbed at 357 - 373 K as a wide

peak with $T_1 = 523$ K, $T_2 = 673$ K and $T_3 = 800 - 810$ K, which corresponds to its adsorption on the surface (T_1) and the formation of oxides of Ni and Cu.

The phase composition of the catalyst changes profoundly after thermal treatment of the Ni - Cu - Cr catalyst on Ce/ θ - Al_2O_3 at 1,473 K for 5 h (Figure 4a). There is a slight bend in the curve of the TPR spectrum at 473 K and the main absorption of hydrogen occurs at maximal temperatures both 773 K and 1,073 K, when Cu(Ni) aluminates are reduced. Cu(Ni) Al_2O_4 crystals are also fixed (reflex 2.42) according to XRD data. If the reduction temperature of the catalyst in the TPR curves is brought to 1,223 K, the adsorption of oxygen in the unheated Ni - Cu - Cr catalyst proceeds at a temperature > 373 K (Figure 4 b).

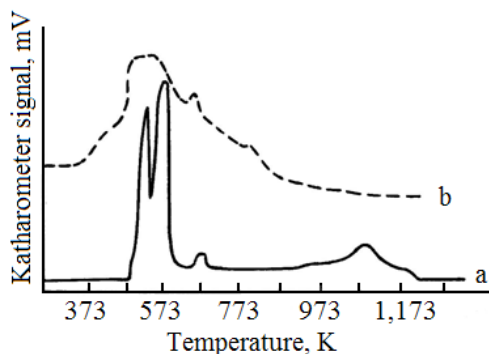


Figure 3: TPR and TPO profiles of the initial Ni - Cu - Cr/2 % Ce/ θ - Al_2O_3 catalyst: a - TPR profile of the initial catalyst, b - TPO profile after TPR up to 1,225 K

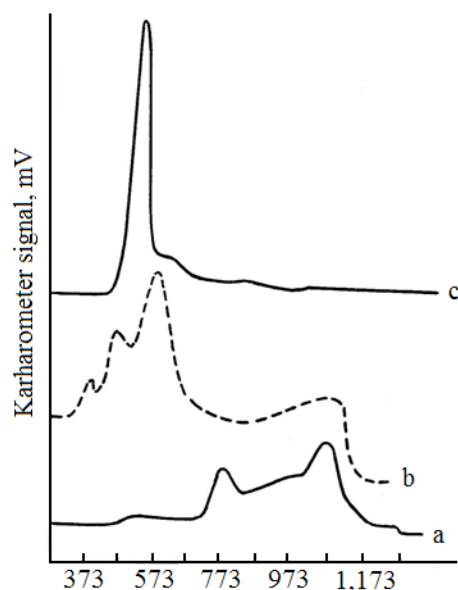


Figure 4: TPR and TPO profiles of the Ni - Cu - Cr/2 % Ce/ θ - Al_2O_3 catalyst: a - TPR profile of the initial catalyst, b - TPO profile of catalyst reduced up to 1,223 K, c - TPR profile of catalyst after treatment in oxygen to 973 K, $T = 1,473$ K, 5 h

Subsequent temperature-programmed reduction of catalyst indicates the absorption of hydrogen only in the form of a single peak (Figure 4b), which means that a mixture of Ni(Cu) oxides is regenerated from its aluminates, which are reduced at 523 K.

According to TPD and TPR data, the Ni - Cu - Cr catalyst is a solid solution of copper and nickel oxides with chromium incorporated in it, on the surface of which superstoichiometric surface of oxygen is adsorbed with $E_{des} = 88 - 89$ kJ mol $^{-1}$, which easily interacts with reducing agents. TPD curves and temperature programmed oxidation data indicate its presence in the catalyst. Under the influence of high temperatures (due to overheating up to 1,473 K during the oxidation of methane and other alkanes), less active Ni and Co aluminates, with the exception of mixed oxides, are formed in the catalyst in an oxidizing atmosphere.

It was shown that the activity of catalysts will remain at a sufficiently high level (methane conversion degree (α_{CH_4}) = 80 – 90 %) if the oxidation of methane and other substances proceeds at temperatures no higher than 973 – 1,000 K, when significant amounts of Ni and Co aluminates are not formed in the composition of catalyst. Under influence of oxygen at higher temperatures (which can occur due to overheating), the amount of mixed oxides in the catalyst decreases in the oxidizing atmosphere according to the TPD data. Less active Ni and Co aluminates are formed during oxidation processes.

Studies have shown that the formed Ni and Cu aluminates can be reduced to the initial oxides or their mixtures under the influence of hydrogen at 973 – 1,223 K. The interaction of the reducing agent (hydrogen) in the TPR experiments with the above oxygen structures occurs easily, starting from 473 and up to 673 K. Adsorption of oxygen again on Ni - Cu - Cr catalysts after the decomposition of oxides occurs at low temperatures (325 K). This indicates a high reactivity of adsorbed and lattice oxygen of dispersed oxides, as well as their mixtures and its ability to easily reactivate.

The ability of the resulting $Cu(Ni)Al_2O_4$ aluminates to convert again to oxides under the influence of hydrogen (Table 2) was used to regenerate the catalyst.

Table 2: Influence of treatment conditions of the Ni - Cu - Cr catalyst on its activity in oxidative conversion of CH_4

Catalyst treatment conditions	Temperature, K		
	Ni Start	Cu $\alpha = 50\%$	Cr $\alpha = 90\%$
Air, 873 K	643	800	973
Air, 1,373 K, 0.5 h	773	923	-
H ₂ , 1,223 K, 0.5 h	663	823	973

The activity of catalyst was determined in the oxidative conversion of toluene, which was a frequently present substance in industrial gas emissions. The catalysts were tested at a space velocity of $5 \times 10^3 \text{ h}^{-1}$, in the temperature range of 523 – 723 K and a toluene concentration of 320 mg m^{-3} . The degree of toluene conversion increases on all catalysts as the temperature rises from 523 to 723 K. The degree of toluene conversion increases from 74 to 98.8 % at a temperature of 673 – 723 K on an optimal Ni - Cu - Cr/2 % Ce/ θ - Al_2O_3 catalyst. A further increase in temperature did not affect the degree of toluene conversion. It was found that the polyoxide Ni - Cu - Cr catalyst supported on 2 % Ce/ θ - Al_2O_3 provides 98.8 % conversion of toluene to CO_2 at optimum temperature of 723 K in the reaction of toluene oxidation at a space velocity of $5 \times 10^3 \text{ h}^{-1}$ and toluene content equal to 320 mg m^{-3} in the initial mixture with air.

The effect of space velocities of the deep conversion of toluene on effective Ni - Cu - Cr/2 % Ce/ θ - Al_2O_3 catalyst was studied. The toluene conversion on the catalyst was studied in the temperature range of 573 – 773 K with a toluene concentration in the initial mixture equal to 320 mg m^{-3} .

Experimental data showed that the toluene conversion degree decreases from 89.5 to 83.8 % on the Cu - Cr/2 % Ce/ θ - Al_2O_3 catalyst at 573 K and increase of the space velocity from 5 to $5 \times 10^3 \text{ h}^{-1}$. The 85.7 % toluene conversion degree was observed on the catalyst at space velocity of $10 \times 10^3 \text{ h}^{-1}$. A similar dependence of toluene conversion is observed at a temperature of 673 K. The toluene conversion degree in the indicated ranges of space velocities is higher than conversion at a reaction temperature of 573 K. The highest conversion of toluene to 98.5 % is achieved at a temperature of 723 - 773 K and a space velocity of $5 \times 10^3 \text{ h}^{-1}$. Toluene conversion decreases both at 573 and at 673 K at higher space velocities ($10 - 15 \times 10^3 \text{ h}^{-1}$).

The effect of toluene concentration in the initial mixture on its conversion on Ni - Cu - Cr catalysts was studied. Increase the toluene concentration in the initial mixture from 100 to 570 mg m^{-3} leads to a slight decrease of the toluene conversion degree on two-component Ni - Cu/2 % Ce/ θ - Al_2O_3 , Cu - Cr/2 % Ce/ θ - Al_2O_3 , and Ni - Cr/2 % Ce/ θ - Al_2O_3 catalysts. The highest toluene conversion degree (up to 98.8 %) is observed on the ternary Ni - Cu - Cr/2 % Ce/ θ - Al_2O_3 catalyst.

4. Conclusions

As a result of the studies, low-percentage oxide catalysts without noble metals for the purification of waste gases from toluene were developed and investigated by TPD, TPR, TPO, XRD, and TEM methods. It was shown that the resulting Ni and Cu aluminates can be reduced to the initial oxides or their mixtures under the influence of H_2 at 973 – 1,223 K. 98.8 % purification is provided on an effective thermal stable polyoxide catalyst while optimizing process parameters (temperature, space velocity, concentration of toluene in the gas mixture) of deep toluene oxidation at a space velocity of $5,000 \text{ h}^{-1}$ in the temperature range of 723 - 773 K at 100 - 570 mg m^{-3} toluene content in the initial reaction mixture.

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