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Development of Technology for Catalytic Neutralization of Toxic Impurities of Waste Gas from Industrial Enterprises

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The results of deep oxidation of toluene on polyoxide nickel-, copper-, chromium-containing catalysts supported on 2 % Ce/θ-Al_2O_3 are presented in the paper. Effect of process parameters (temperature, space velocity, concentration of toluene in a gaseous mixture) on the completeness conversion of toluene (to CO_2 and H_2O) on polyoxide catalyst has been studied. Polyoxide Ni-Cu-Cr catalyst supported on 2 % Ce/θ-Al_2O_3 in oxidation of toluene at space velocity of 5×10^3 h^{-1}, 723 - 773 K and 320 mg/m^3 toluene content in initial mixture provides 98.8 % toluene conversion to CO_2. The presence of CeO_2 crystals and X-ray amorphous clusters (d = 20 – 100 Å) of the oxides of metals of variable valence NiO, CuO, and solid solutions of metals CuO (NiO) on the surface of Ni-Cu-Cr/2 % Ce/θ-Al_2O_3 catalyst calcined at 873 K was installed by X-ray diffraction and electron microscopy.

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 from 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).

It is known that the sorption (adsorption, absorption) and deep oxidation (catalytic, thermal), as well as their combination are the main methods of utilization and neutralization of gas emissions from impurities of harmful volatile organic compounds. From the literature data (Popova et al., 2006), which presents an overview of methods and apparatuses of neutralization of toxic emissions follows that the most economical way to clean of gases with harmful emissions of complex composition is deep catalytic oxidation. 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 that do not contain noble metals or containing their small amounts is an important problem at the present time. The use of palladium catalysts with low metal content or

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catalysts based on mixed oxides is one of the most promising solutions to this problem. The data on studying the process of deep oxidation of toluene on polyoxide nickel-, copper-, chromium-containing catalysts are presented in this paper. Toluene as the main component of emissions the furniture, cable, footwear and other production has been chosen as model substance of neutralization.

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. Ball θ-Al_2O_3 (manufactured by the Boreskov Institute of Catalysis SB RAS, Novosibirsk) diameter of 3 – 4 mm with surface area of 100 m^2/g, bulk density of 0.80 g/cm^3, the mechanical strength of 150 MPa and pore volume of 0.48 cm^3/g was used as a carrier. θ-Al_2O_3 was modified by cerium oxide to stabilize the structure and thermal stability. It forms a surface perovskite $CeAlO_3$ type with alumina that is stable up to 1,373 K (Zheksenbaeva et al., 2012).

Previously, it was investigated the effect of ratio and concentration of elements on γ-Al_2O_3 on their efficiency in oxidation of 1 % CO and 0.5 % CH_4 in air at space velocity 100×10^3 h^{-1} (Altynbekova et al., 2000). Variation of the components in mixture of elements allowed optimizing the chemical composition and ratio of elements in the mixed catalyst (in atomic ratio): Ni : Cu : Cr = 1 : 3 : 0.1. Catalyst composition corresponded to the stoichiometry of oxide in the spinel structure. It was shown that 7-10 % catalysts are optimal when the clusters of metal oxides are formed on the surface and complete uniform impregnation of granulated alumina is achieved.

Toluene content before and after reaction was analyzed on the Crystal – 2000M chromatograph with a flame ionization detector (24.91 Hz) on a capillary column. Column temperature – 433 K, vaporizer temperature – 513 K, rate of hydrogen - 25 mL/min, rate of air - 250 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 - 15×10^3 h^{-1}) and toluene concentration (320 mg/m^3) in the initial mixture (Tungatarova et al., 2012).

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 N_2.

The morphology, particle size, chemical composition of the Ni-Cu-Cr catalysts were investigated by a transmission electron microscope EM-125K at 80,000 magnification by the replica method with extraction using a microdiffraction.

3. Results and Discussion

3.1 Investigation of the activity of Ni-, Cu-, Cr-containing catalysts in the reaction of deep oxidation of toluene

Figure 1 presents the data obtained in the oxidation of toluene in synthesized nickel-copper-chromium oxide catalysts at 723 K and space velocity 5×10^3 h^{-1}. The Figure 1 shows that the nickel-copper-chromium-containing polyoxide catalysts of the deep oxidation of toluene by activity are located in the following order: Ni-Cu-Cr/2 % Ce/θ-Al_2O_3 (98.8 %) > Ni-Cu-Cr/θ-Al_2O_3 (93 %) > Ni-Cu/2 % Ce/θ-Al_2O_3 (85 %) > Ni-Cr/2 % Ce/θ-Al_2O_3 (76 %) > Ni/2 % Ce/θ-Al_2O_3 (57 %).

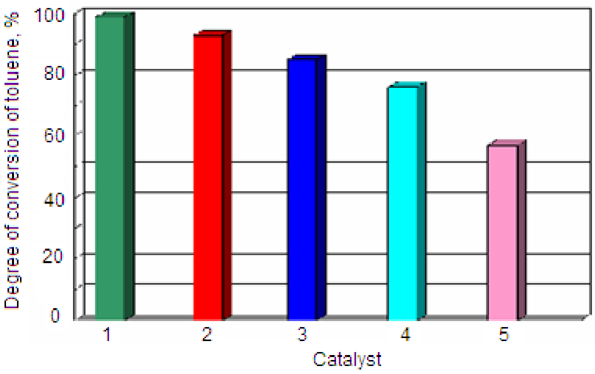

Figure 1: The oxidation of toluene in air on oxide Ni-Cu-Cr containing catalysts: 1 - NiCuCr/2 % Ce/θ-Al_2O_3; 2 - NiCuCr/θ-Al_2O_3; 3 - NiCu/2 % Ce/θ-Al_2O_3; 4 - NiCr/2 % Ce/θ-Al_2O_3; 5 - Ni/2 % Ce/θ-Al_2O_3

It should be noted that comparison of the activity of multicomponent Ni-Cu-Cr containing catalyst supported on alumina modified by cerium with catalyst supported on alumina without cerium showed that the conversion of toluene on the catalyst Ni-Cu-Cr/2 % Ce/θ-Al_2O_3 significantly higher (98.8 %) than on the Ni-Cu-Cr/θ-Al_2O_3 (93 %).

Thus, the highest degree of conversion (up to 98.8 %) of toluene was determined on the multicomponent Ni-Cu-Cr/2 % Ce/θ-Al_2O_3 catalyst supported on alumina modified with cerium, the lowest - on Ni/2 % Ce/θ-Al_2O_3 contact.

Methods of introducing the active components in composition of the Ni-Cu-Cr catalyst for the deep oxidation of toluene to CO_2 and H_2O were investigated. Methods of supporting of the catalytic active phase showed that sequential introduction the components are not optimal for efficiency of supported Ni-Cu-Cr catalyst. The best result was obtained by simultaneously introducing all components in the impregnation solution (see Table 1).

Table 1: Effect of the method of introduction of active components into the Ni-Cu-Cr catalysts supported on Al_2O_3 on the efficiency in oxidation of toluene in air at $5×10^3$ h^{-1}

Method of introducing the components (Ni, Cu, Cr)	The degree of conversion, %, at a temperature, K			
	523	573	673	723
Simultaneous (Ni, Cu, Cr)	73.0	89.0	94.0	98.8
Sequential (first Cr, then the sum of Ni and Cu)	56.0	66.0	80.0	91.0
Sequential (first Ni, then the sum of Cr and Cu)	52.0	62.0	78.0	85.0
Sequential (first Ni, then Cu and Cr)	50.0	61.0	75.0	82.0

Modification of catalysts with small additions of compound with basic character which are introduced into the impregnating solution (Na_2CO_3, KOH and NH_4HCO_3) is one way of obtaining the catalysts with uniform distribution of components.

Effect of process parameters (temperature, space velocity, concentration of toluene in gaseous mixture) on the completeness conversion of toluene (to CO_2 and H_2O) on the Ni-Cu-Cr/2 % Ce/θ-Al_2O_3 polyoxide catalyst was studied. The degree of oxidation of toluene from the variation of space velocities at different temperatures on the Ni-Cu-Cr/2 % Ce/θ-Al_2O_3 catalyst are presented in Table 2. It can be seen that with the increase of space velocity from $5×10^3$ to $15×10^3$ h^{-1} degree of oxidation of toluene reduces from 98.5 to 89.3 %, respectively.

Table 2: Effect of temperature and space velocity on the degree of conversion of toluene on the Ni-Cu-Cr/2 % Ce/θ-Al_2O_3 catalyst

T, K	Space velocity, $×10^3$ h^{-1}		
	5	10	15
	Degree of conversion of toluene, %		
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/m^3

Thus, degree of conversion of toluene to CO_2 reaches the 98.5 – 98.8 % on the Ni-Cu-Cr/2 % Ce/θ-Al_2O_3 catalyst at a temperature of 723 – 773 K and space velocity $5×10^3$ 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 3 shows that increasing the concentration of toluene from 100 to 320 mg/m^3 in the initial mixture with air leads to a slight decrease in the degree of conversion of toluene on the two component Ni-Cu/2 % Ce/θ-Al_2O_3 and Cu-Cr/2 % Ce/θ-Al_2O_3 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 %. Ni-Cu-Cr/2 % Cr/θ-Al_2O_3 catalyst was the most stable.

Table 3: 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%Cu-Cr/2%Ce/θ-Al_2O_3	68.0	67.9
5%Ni-Cr/2%Ce/θ-Al_2O_3	76.6	73.0
5%Ni-Cu/2%Ce/θ-Al_2O_3	85.0	84.0
9%Ni-Cu-Cr/2%Ce/θ-Al_2O_3	98.5	98.8

Note – T – 723 K; GHSV - 5×10^3 h^{-1}

Thus, the optimal conditions of deep oxidation of toluene on oxide Ni-, Cu- and Cr-containing catalysts over 2 % Ce/θ-Al_2O_3 were determined. Degree of conversion of toluene reaches 98.5 – 98.8 % on the Ni-Cu-Cr/2 % Ce/θ-Al_2O_3 catalyst at temperatures of 723 – 773 K, GHSV - 5×10^3 h^{-1} and the concentration of toluene in the initial mixture with air – 100 - 320 mg/m^3.

3.2 The study of polyoxide catalysts based on Ni-, Cu-, Cr- on 2 % Ce/θ-Al_2O_3 by X-ray diffraction analysis

Table 4 shows the results of determination of the phase composition of initial 2 % Ce/θ-Al_2O_3 and Ni-Cu-Cr catalysts on 2 % Ce/θ-Al_2O_3 after preparation under the following conditions: heating temperature - 873 K for 1 h, duration of heating - 5 h at 873 K in air with a consequent increase in temperature to 1,473 K and holding at this temperature for 5 h. Reflections from θ-Al_2O_3, α-Al_2O_3 and CeO_2 (quantitative evaluation was carried out by reflexes 2.31 Å, 1.74 Å, 1.91 Å, respectively) are present in 2 % Ce/θ-Al_2O_3, as well as in the carrier.

Figure 2 shows dependence of the intensity of CeO_2 (1.91 Å), α-Al_2O_3 (1.74 Å), Ni(Cu)Al_2O_4 (1.43 Å) and surface area from heating temperature of the Ni-Cu-Cr/2 % Ce/θ-Al_2O_3 catalyst in air. Intense reflections from the CuO and less intense reflections from the NiO except CeO_2 and θ-Al_2O_3 phases are observed in roentgenograms of the Ni-Cu-Cr/2 % Ce/θ-Al_2O_3 heated at 873 K. Not only crystallization of CeO_2 occurs as a result of heating of the Ni-Cu-Cr/2 % Ce/θ-Al_2O_3 catalyst but the content of α-Al_2O_3 increases sharply, starting from 1,273 K. Significant decrease in the total surface of catalysts takes place due to this process at heating. CeO_2 crystallization process occurs to a lesser degree due to the low content of cerium (only in the carrier).

Promotion of the Ni-Cu-Cr catalyst by Pt and Pd also contributes the phase transformations in catalyst under heating. Weak reflections from the NiO, Ce_6O_{11} as well as $NiAl_{10}O_{16}$ are available in the X-ray data except crystal CeO_2, α-Al_2O_3, CuO, Ni(Cu)Al_2O_4.

Thus, based on the XRD data the presence of CeO_2 crystals and X-ray amorphous clusters (d = 20 – 100 Å) of oxides of variable valence metals NiO, CuO as well as solid solutions of metals CuO (NiO) was recorded during the synthesis of catalyst after heating at 873 K on the carrier surface.

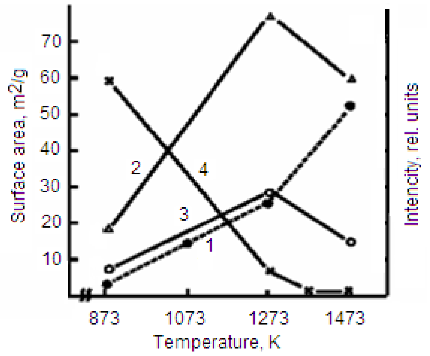

Figure 2: Dependence of the intensity of CeO_2 (1.91 Å), α-Al_2O_3 (1.74 Å), Ni(Cu)Al_2O_4 (1.43 Å) reflexes and the surface area from heating temperature in air for the catalyst Ni-Cu-Cr/2 % Ce/θ-Al_2O_3: 1 - Cu(Ni)Al_2O_4 (reflex 1.43 Å), 2 - relative content of α-Al_2O_3 (reflex 1.74 Å), 3 - relative content of CeO_2 (reflex 1.91 Å), 4 - surface area

Phase transformations occur in the Ni-Cu-Cr catalyst upon heating in air above 1,273 K. Metal oxides react with alumina to form an aluminate $MeAl_2O_4$ type with d = 200 – 1,000 Å. Wherein the surface decreases sharply to 2.5 m^2 (Grigor'eva et al., 2002).

Table 4: Results of the XRD analysis of polyoxide Ni-Cu-Cr catalysts supported on 2 % Ce/θ-Al_2O_3

Catalysts	Promoter, %	$T_{heating}$, K	CeO_2, 1.91 Å	α-Al_2O_3, 1.74 Å	θ-Al_2O_3, 2.31 Å	$NiAl_2O_4$, $CuAl_2O_4$, 1.43 Å	Less intensive phase
$Ni_1Cu_3Cr_{0.1}$		873	13	37	10	-	CuO (2.51, 2.31, 1.85) NiO (2.08, 2.42, 1,48)
		1,273	58	158	5	90	
		1,473	30	120	3	105	
	0.3 Pt	873	10	9	22	-	CuO, Al_2O_3 (2.12), NiO (2.42)
	0.1 Pt	873	14	20	-	-	CuO, Al_2O_3 (2.12), Ce_6O_{11}, Cr_5O_{12} (3.57)
	0.1 Pt	1,073	26	20	10	10	CuO, NiO, Ce_6O_{11}, Al_2O_3
	0.3 Pt	1,473	52	166	5	70	
	0.05 Pd	873	20	13	7	7	CuO, Ce_6O_{11}, Al_2O_3 (2.12)
	0.05 Pd	1,273	45	148	2	55	Pd (2.25)
	0.05 Pd	1,473	60	177	5	105	$NiAl_{10}O_{16}$ (1.99)

3.3 The study of multicomponent oxide catalysts based on NiCuCr over 2 % Ce/θ-Al_2O_3 by electron microscopy

The morphology of the Ni-Cu-Cr catalysts was examined by a transmission electron microscopy at increasing components in the Ni-Cu-Cr catalyst. It was found that single, double and triple metal oxides are formed during complication of composition of the Ni-Cu-Cr catalysts, the particle size of which decreases from 50 - 80 Å (Ce/Al_2O_3) to 20 - 30 Å (Ni-Cu-Cr).

From the data of electron microscopy and microdiffraction (Table 5) is seen that the catalysts contain mainly nanoparticles of oxides (20 – 100 Å) and mixtures thereof, as well as larger, dense particles of aluminates AB_2O_4 and ABO_3 types with size of 200 – 300 Å after heating at 873 K.

When introducing of the Pt or Pd in Ni-Cu-Cr catalyst was also formed two types of particles: fine oxides (60 – 150 Å) and larger aluminates in the case of promotion by Pd with d > 1,000 Å, especially by heating to 1,473 K. Most of the particles is finely dispersed at promotion by platinum, which grow in size to 200 – 500 Å after heating at 1,473 K due to formation of aluminates and chromates. The relative content of large particles of metals aluminates in the Ni-Cu-Cr catalysts increases at promotion by Pt and Pd, and at the high-temperature heating.

Table 5: Data of electron microscopy studies of polyoxide Ni-Cu-Cr catalysts supported on 2 % Ce/θ-Al_2O_3

Catalysts	$T_{heating}$, K	Particle size, Å	Diffraction data
Ni_1-Cu_3-$Cr_{0,1}$	873	20 – 30	$NiCr_2O_4$, $CuCrO_4$, $CuAl_2O_4$, $CuAlO_4$, $NiAl_2O_4$, CrO_2,
		20 – 100	Cr_2O_3,$CuAlO_2$, AlCu, $NiCrO_4$, Cr_2O_3
	1,473	> 200	$CuAl_2O_4$, $NiAl_2O_4$, $CeAlO_3$
Ni_1-Cu_3-$Cr_{0,1}$+Pd	873	100	oxides of Cu, Ni, Cr; CeO_2
		200 – 500 (flakes)	aluminates of Cu, Ni; $CuCr_2O_4$, PdO, Ce_2O_3, CrO_2, $NiCrO_3$ $CuAl_2O_4$, $CuCr_2O_4$,
	1,473	> 1,000	$NiCrO_3$, $CeAlO_3$, oxides of Cu, Ni, Cr, $NiAl_{26}O_{42}Cu_2O$, Ni_2O
Ni_1-Cu_3-$Cr_{0,1}$+Pt	873	60 - 150	oxides of Cu, Ni, Cr, Pt° Cu_2O, Ni_2O, PtO, $NiAl_2O_3$
	1,473	200 – 500 (dispersion, enlargement)	$CuAl_2O_4$, CrO_4, Cr_2O_3, Ni_2O_3 Cu_2O, Pt°, $NiCrO_4$, Ni_2O

Thus, nanoparticles of metal oxides or their mixtures are formed in the initial oxide Ni-Cu-Cr catalyst after decomposition of metals nitrate at 873 K according to electron microscopy and microdiffraction. Process of interaction of elements with the carrier θ-Al_2O_3 to form larger aluminates of copper and nickel AB_2O_4 or ABO_3 types occurs with increasing temperature (Komashko et al., 2002).

4. Conclusions

Polyoxide supported Ni-Cu-Cr/2 % Ce/θ-Al_2O_3 catalyst with desired properties for deep oxidation of hydrocarbons - toluene, xylene, styrene, ethyl acetate, butyl acetate, isobutanol, formaldehyde, acetone, ethanol and others who have severe toxic effects on a living organism and flora was developed. It has been shown that the synthesized polyoxide Ni-Cu-Cr catalyst supported on 2 % Ce/θ-Al_2O_3 provides 98.8% toluene conversion to CO_2 at space velocity of 5×10^3 h^{-1}, temperature of 723 – 773 K and 320 mg/ m^3 content of toluene in the feed mixture.

By X-ray diffraction and electron microscopy was established the presence of CeO_2 crystals and X-ray amorphous clusters (d = 20 - 100 Å) of the oxides of transition metals NiO, CuO, as well as solid solutions of metals CuO (NiO) on the surface of Ni-Cu-Cr/2 % Ce/θ-Al_2O_3 catalyst prepared by impregnation method and calcined at 873 K. Phase transformations occur in the Ni-Cu-Cr catalyst at heating above 1,273 K in air: metal oxides react with alumina with the formation of aluminates $MeAl_2O_4$ type with d = 200 – 1,000 Å with simultaneous decrease of specific surface area.

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