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Catalytic purification of gas emission using complex metaloxide $CuOMnO_2$

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Abstract. The article presents the results of a study of catalytic purification processes from carbon and nitrogen compounds in order to reduce the contamination of surface layers of atmospheric air. The article proposes a method for producing heterogeneous catalysts based on copper and manganese for purification of waste gases from carbon monoxide, nitrogen dioxide and methane. The studied conditions for the preparation of the catalyst by the multistage pyrolysis method in the temperature range from 250-8,500C. The efficiency of using heterogeneous catalysts, based on complex oxides in laboratory conditions, was estimated. The amount of pollutants in the waste gases before and after the catalysis was determined. It has been established that the introduction of catalytic purification to suppress gas emissions will improve the quality of waste gases. In addition, the proposed action will reduce the damage from air pollution. All this will ultimately lead to the stabilization of the ecological situation in the region and the reduction of costs, associated with environmental payments.

1. Introduction

The Tyumen region is a dynamically developing industrial region, the growth of which is accompanied by an intensive technogenic impact on the state of the environment. Anthropogenic influence is aggravated by severe natural and climatic conditions in the regions of gas production.
All over the territory of the Tyumen region there is a rapid growth of background concentrations for all atmospheric pollutants [1]. Data on gross emissions by characteristic pollutants in the region are shown in Figure 1.

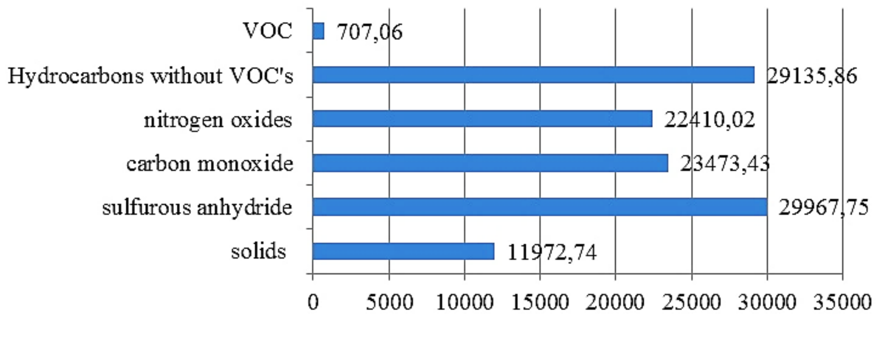


Figure 1. Emissions of pollutants in 2016 from stationary sources, tons per year.

Of the specific substances in the emissions, methane dominated - 22.4 thousand tons, carbon black - 2.3 thousand tons and inorganic dust - 1.3 thousand tons. 406.8 tons of ammonia, 305.5 tons of gasoline (petroleum, low-sulfur), 266.6 Hexane, 233.4 tons of dimethylbenzene (xylene), 205.5 tons of methylbenzene (toluene), 99.2 tons of butane, 86.9 tons of benzene, 58.8 tons of hydrogen sulfide, 57.9 tons of butyl acetate, 32.3 tons of coal ash, 40 tons of acetone, 37.1 tons of formaldehyde, 33.7 tons of ash from shale , 30.5 tons of methanol, 22.6 tons of calcium oxide (quicklime), 21.5 tons of mineral oil, 17.4 tons of ethane (acetic) acid, 14.1 chromium hexavalent, 11.8 tons of hydrogen chloride (hydrochloric acid) [2].

According to [1], it can be established that the greatest amount of pollutants enters the atmosphere of the Autonomous Okrug from enterprises that extract and transport minerals. At present, purification of emissions from gaseous pollutants in industrial plants in Russia is not carried out, but is replaced by dispersion of emissions in the atmosphere, which leads to the accumulation of pollutants in the surface layer of the atmosphere [3-5]

Therefore, the availability of adequate and inexpensive ways of suppressing gas emissions is of important interest for the Tyumen region.

2. Materials and methods

Theoretical foundations of the catalytic purification process are considered [6-10]. Among the methods of obtaining catalysts, preference is given [11-14]. Conditions for obtaining complex metallic oxides by the claimed method have been studied [15-17]

The purpose of this work was to determine the effectiveness of the use of complex metallocosides as catalysts for the thermochemical decomposition of waste gases.

To obtain the most reliable results, the following aspects were considered:

1. The possibility of using pyrolysis to produce a heterogeneous catalyst.
2. Efficacy of using a complex metalloxide catalyst for complex suppression of CH4, CO and NO2 in flue gases.

As a pilot technology for obtaining the catalyst base, was chosen ion exchange for the carboxyl cation exchange KB-4px2 (Table 1) using $Mn(NO_3)_2$ и $Cu(NO_3)_2$ solutions at 298 K under dynamic conditions [18].

Table 1. Physicochemical properties of the cation-exchange resin KB-4px2

Index	KB-4px2
Appearance: grain shape,	Spherical
colour	white
Moisture contents, %	45-60
In the working fraction, not less than, %	40
Size of grains of swollen cation exchanger, mm	0,25-0,5
The total static exchange capacity is 0.1 N. NaOH, meq / cm3, not less than	9,5
Specific volume, cm3 / g, not less than	2,0

The ions adsorption of under dynamic conditions makes it possible to make maximum use of the exchange capacity of the cation exchanger and, consequently, to obtain more regular granules of inorganic material after pyrolysis. The maximum concentration of sorbed ions also exerts a strong influence on the microstructure of the crystals, from which the granule forms and, as a results, on the structure of the volumetric final product. The adsorption of copper and manganese ions is carried out under dynamic conditions on the cation exchange KB-4px2 from the following composition: 1,12 mol/ $dm^3 Cu^{2+}$ и 0,06 mol/ $dm^3 Mn^{2+}$. The obtained composite material "cationite-sorbed copper and manganese ions" is then subjected to heat treatment. The heat treatment regime was chosen taking into account the thermal analysis of the cation exchanger in individual ionic forms and possible complex processes that occur when the polymer material is heated, based on styrene and divinylbenzene. Analysis of the chemical composition of the catalyst and the topography of the powder surface were studied using an AnalysisStation JED-2300 scanning electron microscope with thermal emission (Figure 2). A detailed quantitative analysis is given in Table 2.

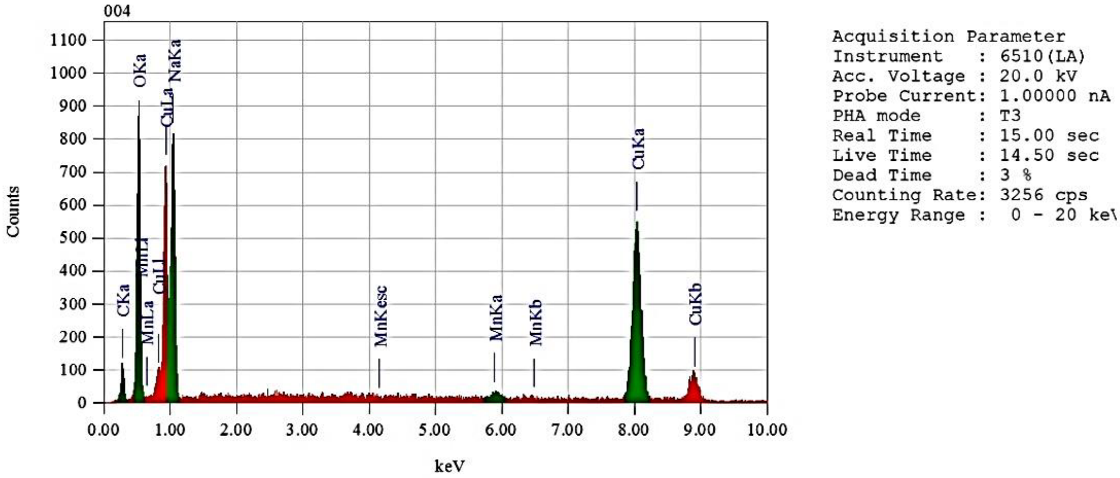
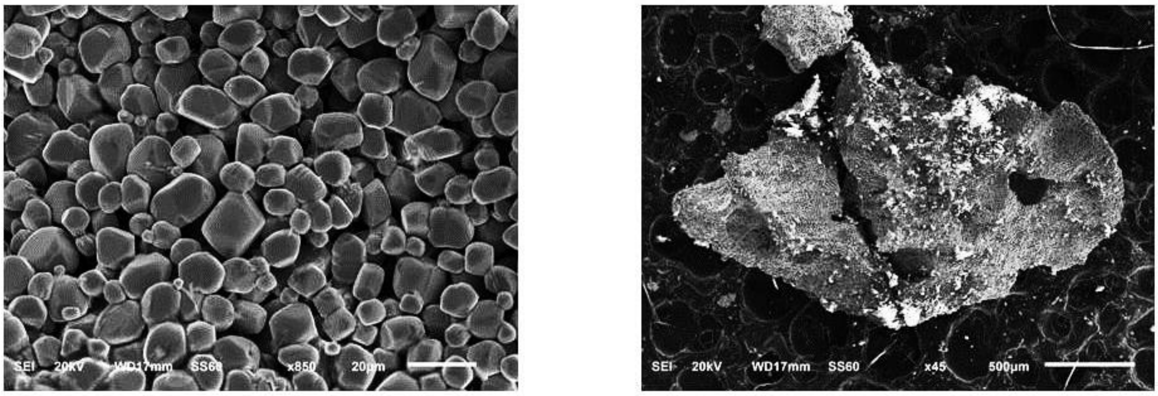


Figure 2. Qualitative analysis of a complex metaloxide catalyst.

Table 2. Content of elements in the resulting complex metal oxide material.

Elements	keV	Mass, %	Counts	Sigma	Atom,%
C	0,277	3,64	591,96	0,02	11,30
O	0,525	12,16	5196,57	0,06	28,34
Na	1,041	10,50	5978,57	0,09	17,03
Mn	5,894	1,08	218,33	0,08	0,74
Cu	8,040	72,61	8292,40	0,45	42,59
Total		100,00			100,00

The catalyst was produced by pyrolysis of saturated ion exchanger in air and then in an atmosphere of a reducing gas [18]. The final product of the reaction is granulate, which in its microstructure is a dense packing of very small crystals of complex oxide CuOMnO2. The structure and appearance of the catalyst are shown in Figure 3.



a b

Figure 3. SEM-micrographs of granulate (a) and the size of a single catalyst particle (b).

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3. Results

The catalyst, which was obtained as a result of pyrolysis, was tested for the efficiency of complex oxidation of the waste gas with methane, carbon monoxide and nitrogen dioxide. For what in the laboratory conditions gas was synthesized by the parameters close to the flue gases of compressor units (Table 3) with a total gas mixture density of 0.575 kg / m3 and a viscosity of 10.65 * 10^{-6}, Pa * s. The working temperature of the catalysis process is 675 K.

Table 3. Concentrations and physicochemical characteristics of gaseous ingredients.

Index	NO_2	CO	Methan
Mass flow of pollutants, Mi g/s	0,150	1,964	5,349
Volumetric concentration,%	0,002	0,026	0,127
Concentration of pollutant, mg/m^3	0,041	0,325	0,900
Density, ρ, kg/m^3	1,340	1,250	0,720
Density at operating temperature, ρ_t, kg/m^3	0,54	0,51	0,29
Viscosity under normal conditions η*10^{-6}, Pa*s	19,28	16,6	10,3
Critical temperature, Tcr, K	179	132,9	190,8

Outgoing gas emissions contaminated with nitrogen oxides, carbon monoxide and the simplest saturated hydrocarbons were sent via a ventilating plant through a heat exchanger and a combustion chamber to a catalytic purification reactor.

During catalytic purification, some amount of carbon dioxide is released, which is determined by the reaction equations 1 and 3 [19,20]:

$$CO \xrightarrow{O_2} CO_2 \quad (1)$$

$$M_{CO_2} = M_i \cdot \frac{\mu_1}{\mu_2}, g / s \quad (2)$$

μ_1, μ_2 - molar masses of the starting component and reaction products, g / mol.

$$CH_4 + 2O_2 \xrightarrow{cat} CO_2 + 2H_2O \quad (3)$$

In the oxidation of methane to 5% of the total weight of the oxidation-prone gas passes into a volatile carbon black, completely settling on the catalyst

$$CH_4 \xrightarrow{t,cat} C + 2H_2. \quad (4)$$

As a result of catalytic oxidation, a steady decrease in the mass of pollutants is observed. Control of contamination concentrations was carried out by the HANK-4 gas analyzer. The results of the measurements are shown in Table 4.

Table 4. Content of pollutants before and after catalytic purification of gas emission, g.

Pollutant	Amount of substance befor catalysis, g	Amount of substance after catalysis, g
NO_2	0,3	0,021
CO	3,928	0,59
CO_2	0	39,9
CH_4	10,808	0,508
Volatile carbon black	0	0,6

4. Conclusion

Thus, the conducted studies of purification of waste gases from harmful pollutants showed that the catalytic method using the developed copper-manganese market allows to reduce pollutant concentrations by an average of 91.09%. The method can be recommended for complex purification of waste gases, compounds of carbon and nitrogen compounds.

The obtained catalysts based on copper and manganese have no domestic counterparts. And they are distinguished by high complex efficiency and low cost, which corresponds to the modern requirements of the catalyst market.

Reduction of concentrations by 91.09% reduces the volume flow of emissions by almost 30 times, and, as a result, reduces the mandatory charges for pollution of the environment by almost 30 times. In addition, the suppression of methane can serve as a prevention of explosion and fire hazards at industrial facilities.

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