

## New Approaches to the Synthesis of the Catalyst Purification of Gaseous Emissions

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For development of effective, stable and inexpensive catalysts of gas purification will be used the natural sorbents of East Kazakhstan.

The primary purpose of research is reduced to the search and production suitable for long-term exploitation and relatively inexpensive catalysts for cleaning of gases with high activity and selectivity that have sufficient mechanical strength, thermal stability, well-developed geometric surface, stability to influence of aggressive environment and low flow resistance.

The innovative technology explains the choice of natural materials of Kazakh deposits for the synthesis of carriers of catalysts for cleaning gases from toxic components, such as oxides of nitrogen and carbon.

### 1. Introduction

The intensive development of advanced technologies in the industry is accompanied by continuous increase in emissions (Jecha et al., 2013). A mandatory requirement for industrial manufacturing is the cleaning of waste gases from toxic substances to the normative level (Efremov et al., 2006). A significant contribution to the pollution of the atmosphere is brought of nitrogen oxides (NO<sub>x</sub>) and carbon monoxide (CO), appearing in the combustion of fuel (Zheksenbaeva et al., 2015). Among the existing methods of the deep cleaning of gas emissions most perspective are catalytic, which are increasingly used because they are quite effective (Tungatarova et al., 2014). The basic factors limiting the widespread use of catalytic purification techniques is the high cost, short life, inability to regenerate contacts (in most cases), and technical complications related with the loading / unloading of the contact mass (depending on the construction of the reactor and form of catalysts).

Zeolite is a unique natural mineral which has the ability to absorb and permanently retain in its structure particles of different substances. Therefore, in such technological processes where the use of synthetic zeolites disadvantageous, great importance is the use of natural materials (Altynbekova et al., 2000). Despite the fact that a high catalytic activity and selectivity of zeolites in many chemical reactions was the cause of intense study on various properties of these catalysts, the nature of the catalytic action of crystalline aluminosilicates yet is studied not enough (Efremov et al., 2000).

### 2. Methodology of carrying out experimental researches

The given work considers opportunity to use natural sorbents of Kazakhstan (zeolites (Z), bentonites (B), and their mixes) as basic components of catalyst carriers of gas purification.

The researches were carried out with the help of optical metallographic microscope Olympus BX 51 for defining grains size and other properties of original natural zeolites and bentonites, as well as catalyst carriers on their basis. Electron microscope investigation was carried out on analytic scanning electron microscope Hitachi SU70 and on reflection electron microscope JSM-6390LV in order to obtain information about composition, structure and other properties of near-surface layers of original components of carriers and samples of catalyst carrier.

To obtain gas purification carriers active components such as copper, nickel, chromium and their mixes were applied with various ratio on zeolite -bentonitic ceramic catalysts carriers that had been produced beforehand. As carriers should have high porosity and complex specific surface for providing the opportunity to apply optimal amount of active component, so the use of ceramics is considered the most reasonable. Catalysts carriers were made in the form of pellets of 3 × 3 mm size by methods of powder metallurgy. The main production operations are preparation of plasticized mass with target characteristics (moldability, rheological properties), extruding of semi-finished products, drying, removal of plasticizing agents and baking of the products.

The obtained carriers were held out in the air for three days and then they were exposed to thermal treatment in muffle electric furnace at the temperature of 500 - 1,000 °C using methods described in the following article (Sadenova et al., 2015), while baking moisture evaporates and physical structure of a carrier is formed due to the baking processes.

Method of obtaining active catalysts by impregnating of the carrier with the solution of transition metals parent salts leads to receiving samples with more complex surface and enables to produce the most diverse catalysts due to variation of active component content and conditions of preparation. Production of catalysts by method of impregnating consists of the following stages: preparation of solutions with necessary concentration, impregnating of the carrier in these solutions according to moisture capacity; drying and baking (Sadenova et al., 2014).

Samples of catalysts were prepared by sorbate impregnating according to moisture capacity with aqueous solution of metal salts of formed and baked zeolite – bentonitic carrier with further drying at the temperature 100 - 120 °C during 1 - 2 h and baking in the air at different temperatures.

Analysis of applied catalysts activity was studied in reduction reaction of nitrogen oxides in the presence of carbon oxide (II). Catalysts activity was studied in the laboratory conditions at the unit of flowing type in the temperature interval 100 - 500 °C. Basic testing was carried out at the volume rate of 3,000 h<sup>-1</sup>. After achieving the target temperature selection of reaction products was carried out. In the first flow CO and NO content was defined on gas detector "KANE 940" (range of measured concentrations 0 ÷ 10,000 ppm).

In the second flow CO<sub>2</sub> and N<sub>2</sub> content was defined on gas chromatograph "Khromatek- Crystall 5000". The constant gas flow rate was kept in the system (Brattoli et al., 2014).

### 3. Results

The study of zeolite surface with metallographic microscope (Figure 1) showed that it consists of clinoptilolite and quartz grains.

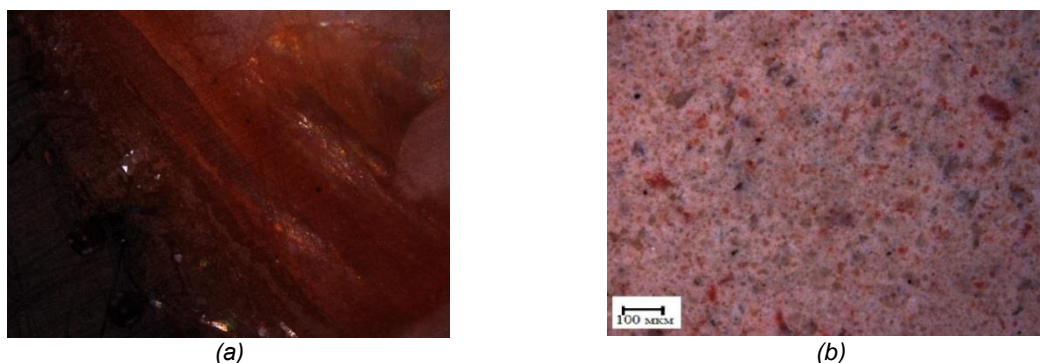


Figure 1: Surface of natural zeolite from Taizhuzgen deposit: a – original; b – crushed

Quartz forms abnormal isometric grains of 0.05 - 0.1 μm having accreted with the grains of other minerals and evenly distributed over the entire area of polished section. Clinoptilolite is presented in red colour. Clinoptilolite grains are evenly distributed over the entire area. Particles contours are sharp, angular which reflect crystalline identity of the studied object. Forms content of greyish tint and silt size are presented by albite angular grains. The surface of crushed zeolite is fine-grained and has clear cut mosaic structure due to grains difference that are characterized by abnormal shape and relatively small size ~ 0.02 μm sometimes reaching 0.1 μm. It was defined during electron microscope investigation that clinoptilolite particles have lamellar habit (Figure 2(a)). Concentration of needle-shaped microcrystals are found in the samples of zeolitized rocks, laumontite is present in the shape of elongate prismatic aggregates formed on the walls of pin holes and cracks (Figure 2(b)).

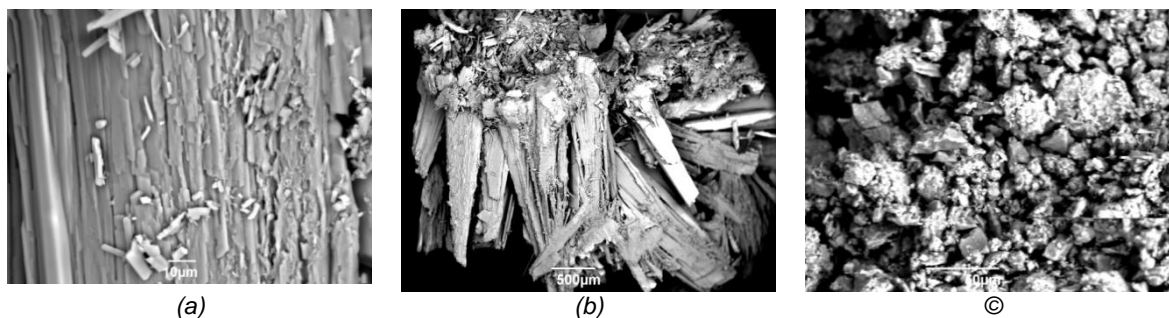


Figure 2: SEM-picture of natural zeolites from Taizhuzgen deposit: a – parent zeolite ( $\times 300$ ); b – parent zeolite ( $\times 30$ ); c – crushed zeolite ( $\times 500$ )

Generally zeolites have complicated microsurface relief formed by crystals and aggregates mostly represented by fine-grained mass (Figure 2(c)).

Main part of bentonite surface (Figure 3) is represented by homogeneous mixture of fine-dispersed clay. Separate quartz grains are observed in the shape of abnormal leaves with sharp contours. It is present mostly in the form of fragmental grains of different rounding.

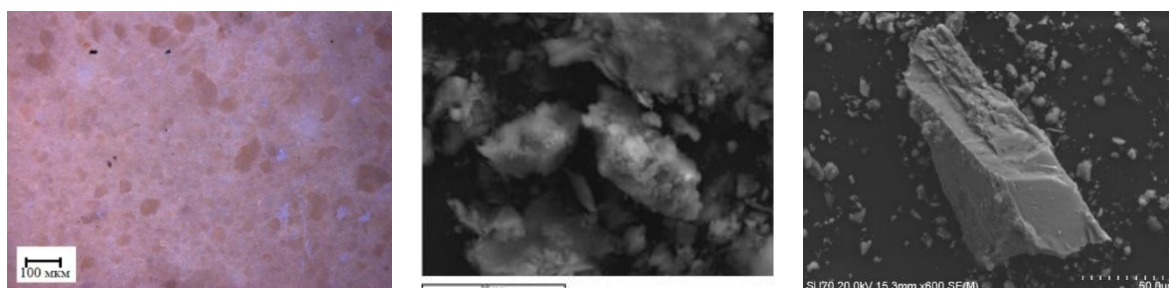
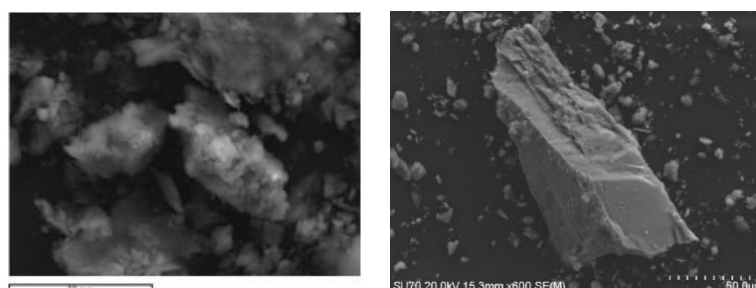


Figure 3: Surface of natural bentonite of Tagan deposit



Quartz grains are clean, of cream greyish color with pink tint, they are cereous and have matt-gloss. The minimal size is 0.03 - 0.04 mm, maximal size - 0.15 mm and medium size is 0.1 mm. Quartz content is 15 – 20 % of the entire surface.

Electron microscope investigation of bentonite showed that the mineral consists of particles of different shapes (Figure 4). Some large particles have lamellated microstructure of the material which influence on sorption properties of bentonite. Microcrystals of montmorillonite look as large and small shells in the shape of leaf aggregates, also aggregates of flaky shape and folded formation can be found. Particles are seen that differ in size and shape they are united into ultramicroaggregates and aggregates with weak- and high – oriented layouts in microblocks. Also pin-holes are noted: most of them are fissured, of different size.

Figure 5 illustrates two-phase system which represents mixture of clayed bentonite and zeolite and looks as large and small flakes united in ultramicroaggregates and microaggregates. Also structureless aggregates of another morphologic type are noted. The sample surface obtained from zeolite-bentonite mixture after pressing in the shape of a pill (load was varied from 0.5 tons to 1.5 tons on hydraulic press) is shown in Figure 5(b). It can be seen that the surface is notable for homogeneity, high dispersion ability and sample's porosity is preserved. In order to develop preparation technology of catalysts it is necessary to know the influence of conditions of production, thermal treatment, and other factors on possible changes of catalyst activity. The activity of the applied catalyst is affected by centers of different nature. In order to define optimal composition. And method of producing thermally stable gas purification catalyst the series of experiments were carried out at various content of active components. The produced catalysts were tested under different conditions.

Literature analysis allowed to find out advantages of producing catalysts by impregnating method which enables to vary the content of active components and to introduce them practically at every stage of preparation. Catalysts were produced by method impregnating zeolite - bentonite carrier with salts of corresponding transition metals according to moisture-holding capacity with further thermal treatment.

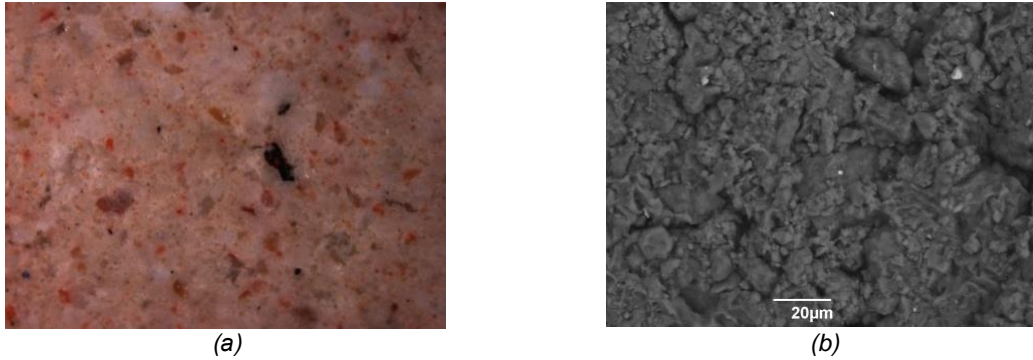


Figure 5: Photos of granulated zeolite - bentonite catalyst carrier samples: a - optical microscopic investigation; b – electron microscope investigation

Mixed two and three component catalysts Cu / Z-B , Ni / Z-B, Cr / Z-B were prepared and applied on Z-B carrier. When conditions for formation, temperature of drying and baling of catalysts were chosen, it was defined that in the solution for impregnating components interact so that aquacomplexes of metals are formed and destruct on the carrier surface at the temperature from 100 to 170 °C (Figure 6). At the temperature 380 - 440 °C thermal decomposition goes on with precipitation of adsorbed water with two endotherm and exotherm effects that corresponds to destruct of metal nitrates and formation of oxides. On the basis of observed data Z-B carrier impregnated with nitrates of salt metals was dried at the temperature of 100 - 120 °C for 1-2 h and was baked in the air at different temperatures.

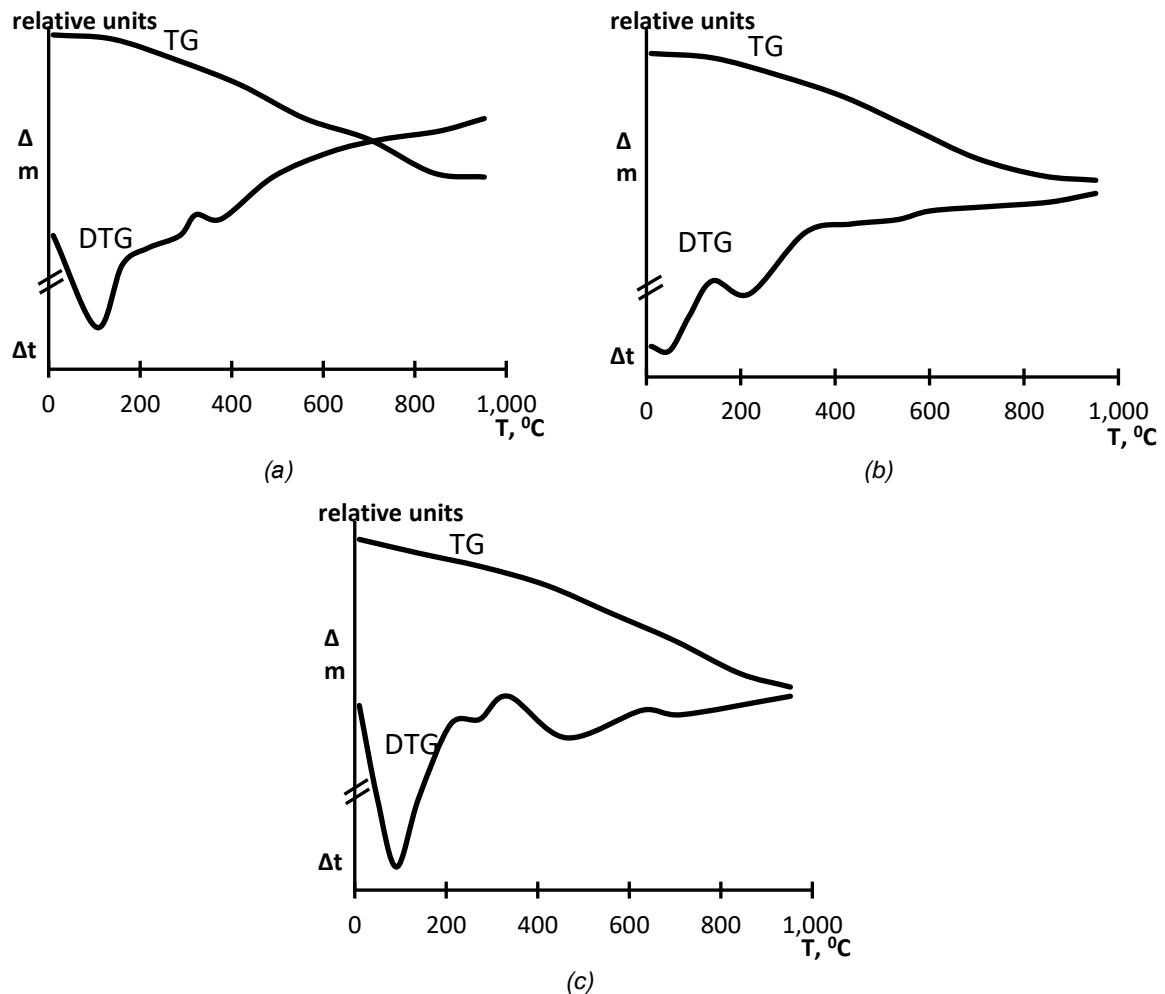


Figure 6: DTG and TG curves Z-B catalyst on the base of: a – copper; b – nickel; c - chromium

The effect of modifying agents applied by impregnating method on granulated Z-B carrier was studied. Figures 7 and 8 illustrate the results of  $\text{NO}_x$  reduction by carbon oxide without oxygen. In Figure 7 it can be seen that the efficiency of unicomponent contacts is lower and CO conversion effervescive in temperatre interval don't exceed 65 %. When two-component contacts were tested CO conversion effervescive increases and rises significantly on three-component catalyst Cu-Ni-Cr / Z-B, where full oxidation reaches 86 % at the temperature 450 °C. This indicates that optimal chemical composition is one of the factors of high catalyst activity of synthesized contacts.

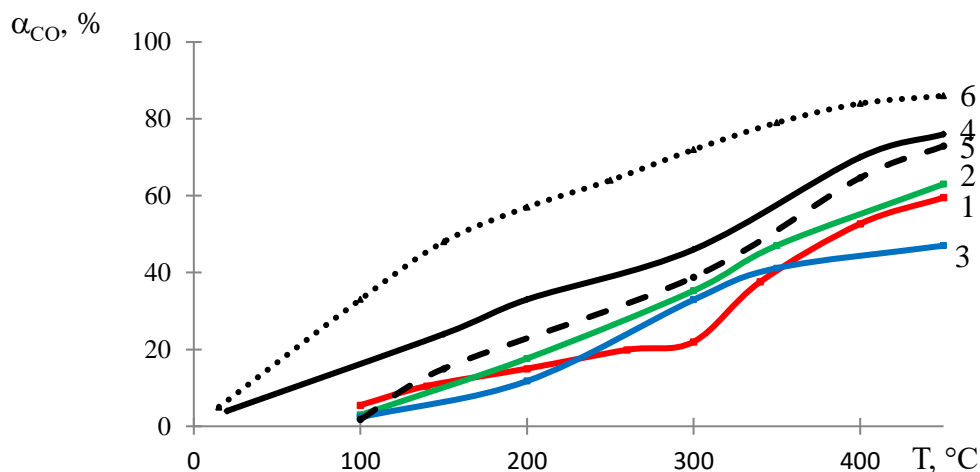


Figure 7: Change of CO reduction value due to temperature of applied catalysts: 1 –Cu / Z-B; 2 –Ni / Z-B; 3 –Cr / Z-B; 4 –Cu-Ni / Z-B; 5 –Cu-Cr / Z-B; 6 –Cu-Ni-Cr / Z-B

According to experimental data conversion effervescive of nitrogen oxide (Figure 8) rises along with temperature increase and reaches 85 % at the temperature of 350 °C for Cu-Ni / Z-B и Cu-Ni-Cr / Z-B catalysts. It is illustrated that in the case of CO oxidation and NO reduction three-component contacts become the most effective. Probably, additional introduction of chromium along with copper and nickel into catalyst compound contribute to more homogeneous distribution of active centers on the catalyst surface and thus its efficiency increases. Besides Cu-Ni / Z-B catalyst also showed high values of  $\text{NO}_x$  activity at the temperature of 400 °C, whereas Cu-Ni-Cr / Z-B reached this value at the temperature of 450 °C. Cr/Z-B catalyst turned out to be inactive under given conditions, its activity was 30 % at the temperature 450 °C.

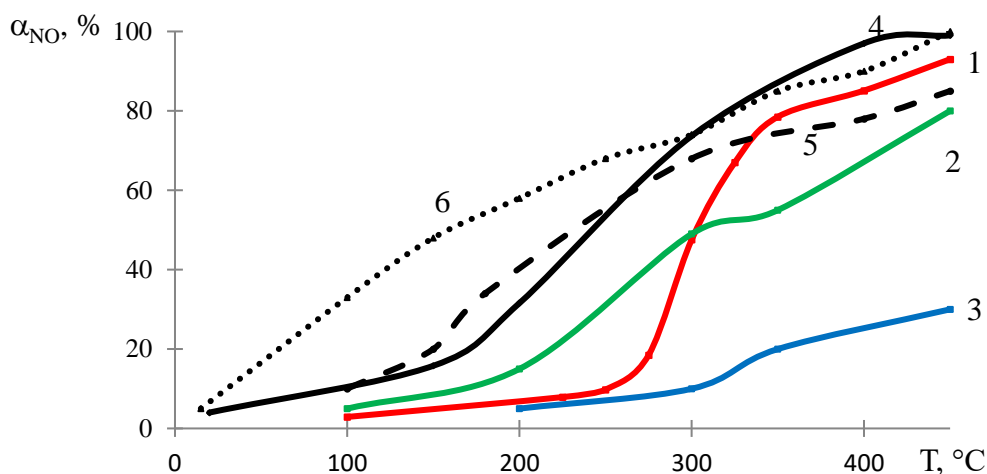


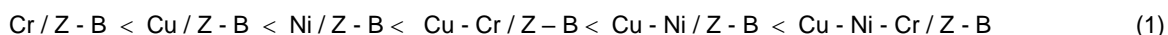
Figure 8: Change of  $\text{NO}_x$  reduction value due to temperature of applied catalysts: 1 –Cu / Z-B; 2 –Ni / Z-B; 3 –Cr / Z-B; 4 –Cu-Ni / Z-B; 5 –Cu-Cr / Z-B; 6 –Cu-Ni-Cr / Z-B

#### 4. Conclusions

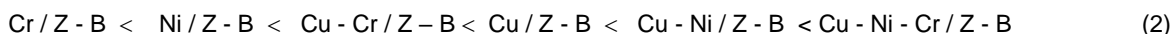
The integrated study of parent natural materials (zeolite and bentonite) and catalyst systems synthesized on their base was carried out. The catalyst systems were synthesized by optical and scanning electron microscopic method and thermogravimetric analysis method. It was studied how catalyst surface and structure changes as their composition becomes more complicated through introduction of the second and third active component into zeolite-bentonite carrier composition. Catalyst activity of synthesized systems was defined at various compositions of catalysts active components. It was proved that effectiveness of one-component contacts in carbon oxide (II) conversion is 40 - 65 %, it increases up to 70 % for two-component contact and reaches 86 % for three-component Cu-Ni-Cr / Z-B catalyst at the temperature of 450 °C. During nitrogen oxide reduction as in case of carbon oxide (II) oxidation, three-component contacts are the most effective. As temperature grows conversion effervesive increases and reaches 85 % at 350 °C for Cu-Ni / Z-B and Cu-Ni-Cr / Z-B catalysts.

As a result of study of produced catalysts on the base of natural sorbents efficiency in reduction reaction of nitrogen oxide to simple nitrogen in the presence of carbon oxide (II), the range of activity is obtained:

CO conversion increases in the range:



NO conversion increases in the range:



High effectiveness of complicate three-component zeolite-bentonite catalyst in comparison with one- and two-component systems can be explained by formation of stable heat-proof active polymetal complexes both on the surface and in the structure of the catalyst itself as it is shown in our article earlier (Sadenova et al., 2016). The obtained data proves that there is the opportunity to develop available and effective catalyst systems on the basis of mineral raw material for nitrogen oxide and carbon oxide conversion in exit gases of different industries.

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