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Modified Natural Zeolites as Catalysts for Catalytic Reduction of NO with CO—Main Components of Exhaust Gases

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Abstract: The study of oxidized-reduced properties of modified natural zeolites from deposits of Georgia—clinoptilolite and mordenite in reaction of reduction NO with H_2, NH_3, CH_4 and especially CO was carried out for the purpose to obtain effective catalyst for afterburning of toxic components of automobile exhaust. The activity of zeolites essentially depends on nature of cation and temperature of reaction and slightly depends on structure of zeolite and ratio of reactants. The introduction of copper and iron ions in preliminary decationated clinoptilolite and mordenite causes growth of conversion degree of nitrogen and carbon monoxides almost on a degree, especially in low temperature interval. The reaction between NO and CO molecules proceeds in coordinative sphere of TM cations through formation of nitrosyl and carbonyl complexes.

Key words: Natural zeolites, NO, CO, reduction, automobile exhaust.

1. Introduction

One of global ecological problem is the pollution of the environment with products of oxidation of nitrogen, carbon and sulfur, contained in exhaust gases and especially in ejected gases of undertaking and thermoelectric power stations (NO_x, CO, NH_3 and hydrocarbons etc.). This problem has been recently more actually because of destruction of ozone layer with nitric oxide except the formation of smog and "acid" rains.

Each year, by burning of hydrocarbons, hundreds of millions tons of four main pollutants are released into the atmosphere—nitrogen oxides, carbon monoxide(II), sulfur dioxide and particulate matter. For example, carbon monoxide—one of the major toxins released into the atmosphere as a result of natural disasters (volcanic eruptions, wildfires) and human activity (gas emissions from industrial enterprises and transport).

Therefore, in the earth's atmosphere, it is thrown mostly carbon monooxide—300 million tonnes (of which 56%-62% are accounted for motor vehicles), 50 million tons of NO_x released with the combustion products and 25 million tons of emissions of the chemical industry. The proportion of nitrogen oxides and carbon emissions is about 60% [1, 2]. However, automobile exhaust gases contain approximately 280 compounds, the most toxic not only nitrogen(II) and carbon(II) oxides, but formaldehyde and phenol, 3,4-carcinogenic benzpyrene and other polyaromatic substances, compounds of inorganic lead.

To decide the automotive emissions' problem and contamination of air, it has been developed a variety of methods and ways that permitted to reduce the amount of emissions or decrease their toxicity.

These methods are the absorption and adsorption, thermal afterburning, biochemical and plasma

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methods and the universal thermo-catalytic cleaning methods. The advantage of catalytic methods is that they allow to convert contaminants into harmless, providing an opportunity to recycle gases with low initial concentrations, achieve high degrees of purification, carry out the process continuously, and avoid the formation of secondary pollutants. The use of catalytic methods are often limited by the difficulty of finding and manufacture the suitable for continuous operation, and quite cheap and effective catalysts. The catalytic oxidation of CO to CO_2—the most realistic and promising method for purifying gases from CO, but if afterburning of CO carries out simply, reduction of NO_x to N_2 will be a difficult task. It is known that nitric oxide (NO) is thermodynamically instable with respect to N_2 and O_2: (i.e. for reaction $2\ NO \rightarrow N_2 + O_2\ \Delta G < 0$). However, the most obvious method of removing NO is catalytic decomposition. From a great number of heterogeneous contacts studied in the conversion of nitrogen oxides, the most effective catalysts till now were Cu-containing zeolites [1-6].

Existing methods for the catalytic purification of waste gases from nitrogen oxides are based on the reduction of NO_x with such compounds as ammonia, hydrocarbons, carbon monoxide and others. For a practical use in this process, only those catalysts are suitable, which remain active in the presence of oxygen, and being a competitor of the interaction of NO_x with carbon monoxide [7]. Therefore, a large excess of oxygen greatly reduces NO_x conversion. However, it found that on some catalysts with rise of oxygen concentration, the conversion of carbon monoxide is increased [8].

In practice, the catalytic purification is the most effective and realized by the use of expensive metals, such as platinum, rhodium and palladium, deposited on neutral carriers (about 50% of extractive platinum is used up on catalytic neutralizers). They best meet the requirements of the gas purification catalysts: high catalytic activity at low temperatures and high volumetric speeds of passing mixtures and insensitivity to the majority of catalyst poisons. Carriers have a honeycomb structure and are mostly made from synthetic ceramic.

As substitutes for catalysts of platinum group, they have been studied intensively complex oxide systems. Highly active catalysts are oxidizing phases with perovskite structure and spinel. Among them are considered to be perspective cuprates of elements: alkaline earth, rare earth and heavy elements, which show high catalytic activity in the conversion of carbon monoxide and nitrogen oxides in non-toxic products [9-11]. Some of them possess high-temperature superconductivity, their structure and many properties have been well studied, which allows more specifically examine some features of their structure due to the catalytic activity. However, the practical application of the cuprates and other perovskites is constrained by the fact that, despite the significant number of researches, questions of the nature of their catalytic activity is not entirely clear [11].

Among the other various adsorbents and catalysts (oxides of titanium, vanadium, intermetallic compound of platinum group and others), synthetic and natural zeolites are more active and selective with respect to corrosive CO, NO_x, SO_2 and H_2S etc.. From the synthetic zeolite materials, the promising was to use the neutralizers obtained by supporting of Fe or Cu ions on pentasils: almost 90% NO_x is converted into N_2 at 350 °C [12-14].

Natural zeolites—a relatively new type of minerals whose use on an industrial scale began only in the 60-ies of XX century. Up to this time in the industry, people usually used the synthetic analogs of natural zeolites. Practical use of natural zeolites induced by discovery in the early 1960s of large deposits in the United States, Japan, former Soviet republics and some other countries. The unique properties of zeolites as adsorbents and ion exchangers are determined by the structural features of the crystal lattice, in which up to 50% of the volume, there are interstices and channels. Experimental-industrial testing of the properties of zeolites proved the possibility of their widespread use as catalysts in a variety of industries, agriculture and ecology. Such natural minerals as clinoptilolite, shabazite, mordenite are characterized by high stability against acids, mechanical and thermal loading, which are accessible and cheap in comparison with oxide catalysts.

Thereby, the main aim of the work is the investigation of possibility of nitric oxides' catalytic neutralization with carbon monoxide, ammonia, hydrogen and methane on cation-modified natural zeolites, such as clinoptilolite and mordenite.

The possibility of catalytic neutralization of NO and CO by using inexpensive, accessible and easy-regenerating catalysts, prepared on the basis of clinoptilolite has been studied in Tbilisi State University for several years and described in a number of papers [15-18]. During the last years, the modernization of catalysts was carried out mainly at the expense of the simplification of preparation methods and search and modification of other natural zeolites.

2. Experimental Part

2.1 Catalysts Preparation

The catalysts were prepared by treatment with complex salts of iron and copper of preliminary decationated and dealuminate zeolite clinoptilolite (CL) from deposits of Dzegvi (Georgia) and mordenite (MOR) from Ratevani deposit (Georgia). The content of initial samples there are in Table 1.

Reagents—solutions of HCl and KOH (NH_4OH), freshly made ammoniac solutions of Cu-contained, Fe-contained salts with different concentration. The chemical composition of samples was determined by chemical analysis, AAS and flame photometry. The state of surface and the preservation of the crystal structure of obtained systems were controlled by X-ray with Cu Kα emission line.

The applied processing method was as [15, 17]:

(1) Washing of grinded natural samples of CL and MOR with weak alkali solutions at room temperature and drying;

(2) Threefold processing with 1 N hydrochloric acid at 353-373 K during one hour;

(3) Washing and drying at 393 K;

(4) Repeated processing with decinormal solutions of ammoniac complexes of corresponding cations;

(5) Washing and drying at 393 K and thermal treatment at 653-673 K during 6 hours in dry air.

The chemical composition is in Table 1.

2.2 Study of Catalytic Activity

Catalytic measurements were carried out on catalytic microflow installation with immovably fixed catalyst bed and varying temperature within 423-773 K, reagent flow rate in the range 200-500 h^{-1}, volume and degree of samples granulation from 1.0 mm to 0.25 mm. The catalyst was preliminary dehydrated in dry air flow at 723 K.

Table 1 Chemical composition of studied zeolites.

Sample	Chemical content in oxide form
CL	$0.51Na_2O·0.17K_2O·0.75CaO·0.30MgO·0.16\ Fe_2O_3·Al_2O_3·8.48SiO_2$
DeCL*	$0.12Na_2O·0.15K_2O·0.44CaO·0.18MgO·0.09Fe_2O_3·Al_2O_3·19.88SiO_2$
HCL	$0.43Na_2O·0.18K_2O·0.76CaO·0.28MgO·0.11Fe_2O_3·Al_2O_3·5.34SiO_2$
CuDeCL	$0.09Na_2O·0.11K_2O·0.11CaO·0.12MgO·0.36CuO·0.06Fe_2O_3·Al_2O_3·19.00SiO_2$
CuFeDeCL	$0.06Na_2O·0.08K_2O·0.06CaO·0.12MgO·0.36CuO·0.22Fe_2O_3·Al_2O_3·22.04SiO_2$
MOR	$0.11K_2O·0.42Na_2O·0.47CaO·Al_2O_3·9.4SiO_2$
DeMOR*	$0.06K_2O·0.19Na_2O·0.34CaO·Al_2O_3·8.6SiO_2$
CuDeMOR	$0.16K_2O·0.16Na_2O·0.26CaO·0.14CuO·Al_2O_3·8.6SiO_2$
CuFeDeMOR	$0.16K_2O·0.16Na_2O·0.22CaO·0.11CuO·0.08Fe_2O_3·Al_2O_3·9.4SiO_2$

* De—decationated sample.

As model used the gas mixtures with content: NO—0.2-1.5 vol.%; CO—0.6-2.0 vol.% and water vapor—5.00 vol.%. The total content of N_2O, NO_2 and O_2 was less than 2 vol.%.

Preliminary treatment of catalyst was carried out by dehydration in a flow of dry air at 523 K. The partial pressure of one of reagents is varied during the experiment, at the same time, the partial pressure of others is stayed permanent, but the common pressure stays practically constant at the expense of insertion in system of the defined amount of air. The composition of initial reagents and obtained products was analyzed by gas chromatography, using helium as carrier gas, molecular sieve 13X and Porapac G or R as chromatographic phases. The rate of NO reduction was calculated on the base of volume flow of gas mixture and content of N_2 and/or N_2O in mixture after reactor.

3. Results and Discussion

3.1 The Temperature Dependence of Catalytic Activity of Studied Samples in Reduction of NO

According to obtained data CL and in the less degree MOR in natural, hydrogen and cation-modified forms display the activity in following reactions: NO_x + CO (1); $NO_x + NH_3$ (2); $NO_x + H_2$ (3) and $NO_x + CH_4$ (4). In low-temperature region, the sharply differ on reducing ability, but in high-temperature interval, initial CL and MOR are more active in selective catalytic reduction of NO by ammonia (Fig. 1). This activity is explained by occurrence of impurities of Transition Metals (TM) in natural zeolites, especially Fe^{3+} in oxide or cationic form. These results are in accordance with literature data [19] that Fe^{3+} cations are more active in reaction (2). The introduction of copper cations in CL and MOR give two effects—reduce the temperature of conversion and in the same time increase the conversion degree. The study of reactions (1-4) on Cu-exchanged samples shows that these reducing agents on their activity located in line: CO > $NH_3 > H_2 > CH_4$ (Fig. 2).

Practically, the same catalytic data were obtained for CuDeCL, promoted with Fe^{3+} ions (Fig. 3). CuFeDeCL shows the smallest activity in reaction (4) and NO_x decomposition. Reactions (2) and (3) are characterized with parallel run of activity curves. Two temperature intervals were determined in NO reduction with CO: from 400 K till 573 K, the linear dependence of conversion degree on temperature is observed, then sharp rise of conversion, which reaches 92% at 623 K (Fig. 3).

The authors find that introduction of Cu^{2+} ions in Fe-contained zeolite causes the displacement of Fe^{3+} in more hard-to-reach positions in zeolite channels, but Fe^{3+} ions, inserted in Cu-exchanged CL and MOR, vice-versa, can't shift copper cations. Since the copper

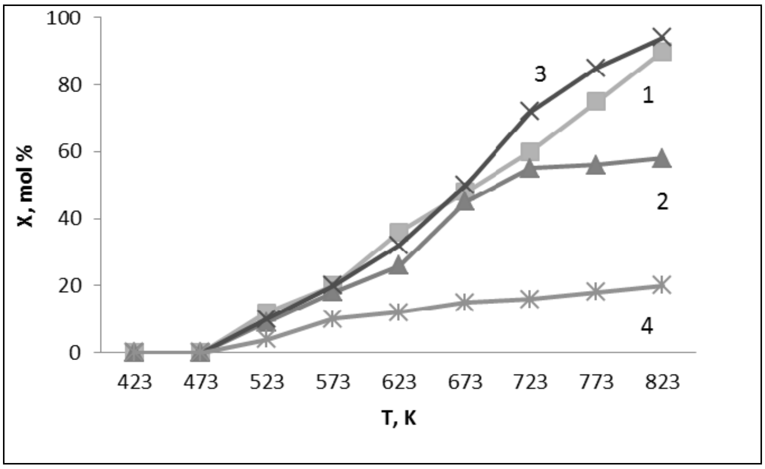

Fig. 1 The temperature dependence of converse degree in reduce of NO with H_2 (1), CO (2), NH_3 (3) and CH_4 (4) on initial CL.

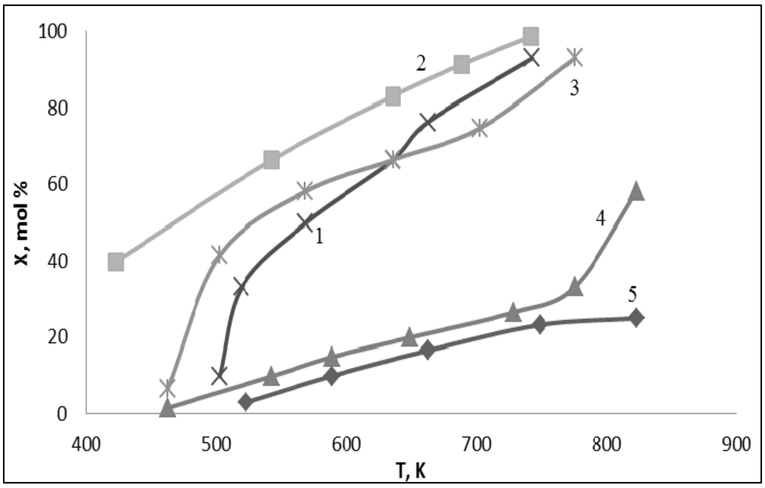

Fig. 2 The temperature dependence of converse degree in reduce of NO with H_2 (1), CO (2), NH_3 (3), CH_4 (4) and NO_x decomposition (5) on CuDeCL.

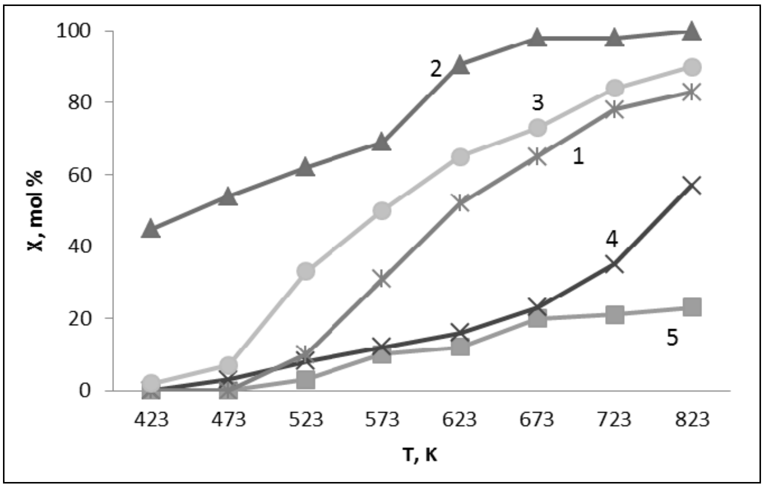

Fig. 3 The temperature dependence of converse degree in reduce of NO with H_2 (1), CO (2), NH_3 (3), CH_4 (4) and NO_x decomposition (5) on CuFeDeCL.

ions have ability to displace iron from its positions, the sequence of introduction of these ions in zeolite structure does not matter. Obtained results about promoting action of Fe^{3+} on Cu-exchanged zeolite are in accordance with literature data [20].

3.2 The Influence of Ratio NO/CO on Conversion Degree

To establish the influence of reactants NO and CO ratio on products yield, it was chosen the reaction (1) as more low-temperature, effective and practical from environmental point of view, since its realization gives possibility to clean the exhaust gases from more toxic components. The ratio of NO and CO have a meaning for way of reaction and obtained products. It was found that maximal conversion in selective catalytic reduction of NO was achieving at stoichiometric ratio NO:CO, equal 1:1.15. At ratio less than stoichiometric, at 573 K reaction carried out with intermediate formation of N_2O.

3.3 The Influence Specificity of Zeolite Structure and Nature of Exchange Cations on Catalytic Activity of CL and MOR

So, the data show that acid decationation of CL and MOR results in decrease of catalytic activity, but treatment with ammonia causes the increase of activity to compare with untreated samples. The introduction of copper and iron ions in preliminary decationated zeolites induces increase of conversion degree of carbon and nitrogen monoxides almost on one order of magnitude, especially in interval of low temperatures. CuDeCL and CuFeDeCL, CuDeMOR and CuFeDeMOR show maximal conversion at 423-773 K, i.e., the temperature range shifts in low temperatures. The main products of reaction (1) are molecular nitrogen and carbon dioxide, the conversion degree reaches 95%-98% at 673 K. It was obtained the following line of activity for all studied samples: DeMOR < DeCL < MOR < CL < HMOR < HCL < CuDeMOR ≤ CuFeDeMOR < CuDeCL ≤ CuFeDeCL.

This dependence shows that though the structure and content of zeolite phase in ore (85% in CL and 60% in MOR) influence on catalytic activity in some degree, the determining factors are the nature, location in zeolitic structure and charging state of substituting cation of transition metal.

At low temperatures, binary zeolite samples possesses more high and stable catalytic activity in interaction reaction of NO and CO, than vanadium-contained, molybdenum-contained and titanium-contained catalysts. CuFeDeCL and CuFeDeMOR show high stable activity in 523-773 K temperature intervals (Fig. 4). The complete reduction of NO reached at 653 K, the selectivity of reaction in regard to N_2 is 88%-92%, and it is carrying out according to scheme: $2NO + CO \rightarrow N_2 (N_2O) + CO_2$.

3.4 The Presumable Mechanisms of Oxidative Catalytic Reactions on Cu-Exchanged Zeolite

Well-defined opinion about presumable mechanism of catalytic action of copper contacts in zeolite matrix in oxidative catalysis is absent in literature till now. Zeolites are characterized with non-ordered distribution of aluminum, silicon and exchanged atoms, so catalytic centers can't be homogeneous. The most of suggested mechanisms are based on oxidative and auto-reductive ability of copper ions according to scheme: $Cu^{2+} \leftrightarrow Cu^{+}$. According to Shutilov R. A. [21], rehydration of Cu^{+}-containing samples does not cause direct Cu^{+} oxidation to Cu^{2+}, but favor in latter process when O_2 is used as oxidant. The lightness of this transformation explains the specificity activity of Cu-exchanged zeolite [22]. On the other hand, the formation of copper clusters on surface or in big channels of zeolite structure is necessary for oxidative reactions [22, 23].

Thus, it is assumed that at least part of copper ions exists as $[Cu^{2+} OH^{-}]^{+}$ or $[Cu^{2+} O^{-}]^{+}$ complexes at small content of substitution cations (about 0.1 mole per 1 mole Al_2O_3), and they are more active in oxidation reactions. Cu^{2+} of these complexes converted in Cu^{+} during vacuumization or at high temperature. At high content of copper there are copper oxocations

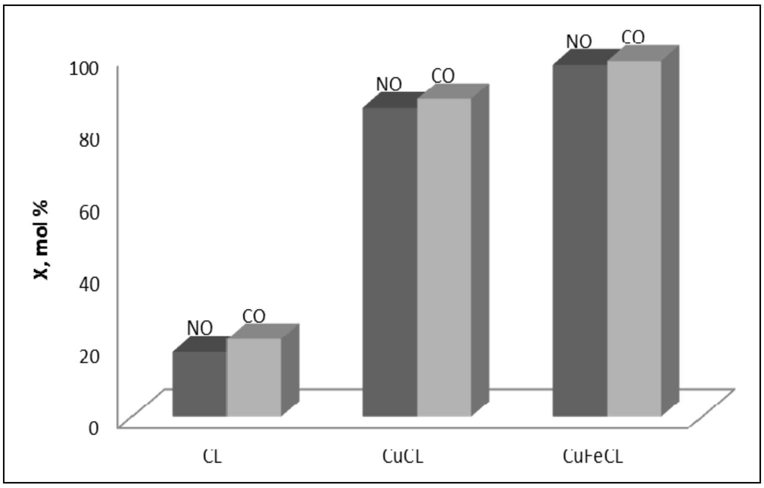

Fig. 4 The comparative activity of CL, CuDeCL and CuFeDeCL in NO and CO in joint conversion at 623 K.

[Cu^{2+}-O^{2-}-Cu^{2+}] in zeolite structure, which also are the active catalytic centers. The ions of Fe also take part in oxidation process, as similarly to copper, the transfer $Fe^{3+} \leftrightarrow Fe^{2+}$ easy occurs. It is supposed that reaction between NO and CO carried out in coordination sphere of these transition metals by formation of nitrozil and carbonil complexes, because of Fe^{3+} and Cu^{2+} cations, located in active cationic positions of zeolite possess the high coordinating ability that determine the catalytic activity. The implications of this coordination mode on the possible molecular mechanism of the catalytic conversion of NO over Cu-exchanged catalysts were discussed [24, 25].

3.5 The Practical Use of Worked out Samples

As a result of laboratory study, it was found that developed on the base of Georgian natural zeolites—CL and MOR were developed the polyfunctional catalysts with exchanged cations of copper and iron, which are characterized by properties:

- They adsorb exhaust gases at room temperature, thanks to high porosity and specific surface;
- Show more high activity and selectivity in joint conversion of CO and NO at lower temperature (420-673 K) to compare with known catalysts on the base of platinum, palladium and rhodium;
- Regeneration of used catalyst carried out by thermal treatment at 673-723 K in flow of dry air;
- The regime of catalyst's work—temperature of conversion beginning at 423 K, degree of NO—45% and CO—63%. At 673 K, conversion degree of NO—98.5% and CO—100%. Products of conversion are molecular nitrogen and carbon dioxide.

Laboratory tests show that worked out copper catalyst is better than known catalysts in some parameters, such as low temperatures, regeneration ability with thermal treatment on air, action without self-heating of system, simplicity and cheapness of initial materials and preparation.

The main lack—it surrenders to existing catalysts in mechanical durability—the tablets break down under vibration. So, the principal modification is selection of according binding agent, which increases the durability without decrease of activity.

CuDeCL and CuDeMOR may be successfully used without binders for afterburning toxic NO and CO as the components of industrial and boilers emissions, because of the container with catalyst motionlessly fixes in ejected tube and don't undergoes to vibration.

It should be note that the method of neutralization of toxic components of exhausts gases with offered zeolite catalysts especially actual as one of ways of decision the problem of "cold start". Three-routed catalysts of automobile exhausts, which are the combination of Pt, Pd and Ro, applied on aluminum oxide or synthetic ceramic, give the possibility to decrease significantly the contamination. But they begin to work at 473-523 K, and so far, as the temperature doesn't reaches these meanings, organic compounds, most part of which are alkenes and aromatics, don't oxidized to CO_2 and H_2O. As a result, 60%-90% of exhaust generated during "cold start" when temperature on catalyst is low, turn out in atmosphere and pollute it. But zeolite catalysts as high-porous systems successfully adsorb and hold reagents until temperature rise and reduction begins.

4. Conclusion

It was shown that the activity of zeolitic catalysts in NO catalytic reduction with CO essentially depends on nature of cation and temperature of reaction and slightly depends on structure of zeolite and ratio of reactants. The introduction of copper and iron ions in preliminary decationated clinoptilolite and mordenite causes growth of conversion degree of nitrogen and carbon monoxides almost on a degree, especially in low temperature interval. The reaction between NO and CO molecules proceed in coordinative sphere of TM cations through formation of nitrosyl and carbonyl complexes.

As regards the practical aspects of this study, the lowering temperature of the conversion of nearly 120 K for copper contained clinoptilolite compared to the catalysts used for post-combustion exhaust gas are the basic advantage of the studied catalysts. The method of neutralization of toxic components of exhausts gases with offered zeolite catalysts is especially actual as one way to decide the problem of "cold start".

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