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Catalytic reduction of nitrogen monoxide with CuZSM-5 catalyst

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ABSTRACT

This study is on the reduction of nitrogen monoxide with CuZSM-5 catalyst of copper oxide compounds modified with zeolite of a silica concentration of 1.5% in mass. The reactions of NO with catalysts composed of mordenites (0.75% CM, 1.5% CuM and 2.2% CuM) were studied and the result showed that these compounds are not active. The reaction of NO with CuO and CuO/ γ -Al₂O₃ compounds was also studied. The reduction of CuO was observed at all temperatures of the experiment. An increase in CuO concentration in the CuO/ γ -Al₂O₃ catalyst of 0.5 to 1.5% by mass increased its activity. The rate of reaction of NO with CuZSM-5 catalyst was higher than that with the CuO/ γ -Al₂O₃ catalyst. Results obtained showed that the CuZSM-5 modified catalyst is more active and therefore can be useful for the purification of the emissions of nitrogen monoxide. This work can contribute to the fight against environmental pollution.

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KEYWORDS

Nitrogen monoxide;
Catalyst;
Reduction;
Zeolite.

INTRODUCTION

One of the most serious problems of our time is that of environmental protection. Waste from manufacturing industries, emissions from energy plants and transportation result in a considerable pollution of the environment^[1]. Toxic elements contained in gaseous emissions that act very rapidly are made up of nitrogen oxides mainly. Several methods are used in reducing the concentration of NO in gaseous emissions. One of the simplest of these methods, which is carried out industrially, is the catalytic reduction of nitrogen oxide. The product of this reaction is N₂, a non-toxic element. CO,

which is equally a toxic compound, occupies a privileged position among these reducing agents. The reduction of NO by CO results in the simultaneous elimination of two toxic elements, that is, NO_x and CO. Catalysts of the monoxide reduction reaction were first of all oxides of precious metals and of complex systems^[2]. Their low mechanical stability, their variable composition as well as high cost gave rise to the use of copper oxides compound catalysts. The drop in the activity with time of these copper oxides catalysts in the process makes the search for better catalysts a necessity and was the basis of our search.

The systematic study of ZSM-5 was carried out by

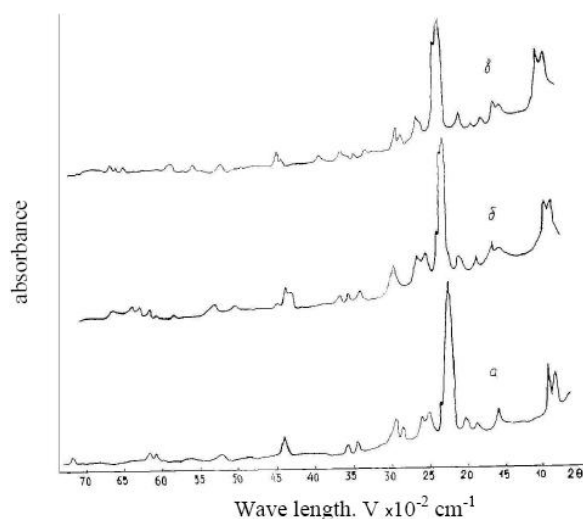


Figure 1 : Diffraction patterns of the CuZSM-5 catalyst. (a) after calcination at 500°C ; (b) after it has been used; (c) after reduction by the CO

Sato et al.^[3] and Iwamoto^[4]. Gazan-Zadeh et al.^[5] studied the activation conditions of Y type zeolitic catalysts containing Ni, Cu, Co and Cr transition elements. They showed that these catalysts displayed various activities in their reactions at temperatures ranging from 100 to 450°C. The introduction of the second transition element into the zeolites caused a significant increase in the catalytic activity. Chipiro^[6] showed that zeolite samples could be classified according to their activity (for 1 g of catalyst) in the order: Ru > Rh > CoNi > CuNi » CrNi > Co > Cu » Cr > Ni.

The CuY zeolite is more active in CO oxidation with O₂ than in the reaction with NO. Among the oxides of transition metals of the 4th period, the most active in the nitrogen monoxide reduction reaction is CuO^[7]. Iwamoto et al.^[8] reported that it is possible to use the CuZSM-5 catalyst to render the exhaust gases of diesel engines non toxic and compare the activity of this zeolite with the CuO/γ-Al₂O₃ catalyst. They showed that at temperatures ranges of 164 to 300°C; CuZSM-5 zeolite showed a high activity level that it maintained even at high voluminal speeds (> 10.000 h⁻¹). In the presence of oxygen, the NO reduction speed increased. It was supposed that this was due to the formation of NO₂ whose reduction speed is higher than that of NO. At low temperatures (300-500°C), all the above cited zeolites undergo partial or total deactivation.

The aim of the present study is the catalytic reduc-

TABLE 1 : Concentration of the reagents and products of the reaction of NO with the different zeolites at the exit of the reactor (mol %); 1g of zeolite; 4.45 mol NO

Type of zeolite	Reagents and products	Temperature°C		
		100-500	100-400	440
0.75 % CuM	NO	4.45		
	N ₂	0		
	O ₂	0		
1.5 % CuM	NO	4.45		
	N ₂	0		
	O ₂	0		
2.2 % CuM	NO	4.45		
	N ₂	0.10		
	O ₂	0		
CuZSM-5	NO		4.45	3.65
	N ₂		0	0.40
	O ₂		0	0

tion of nitrogen monoxide with CO using a CuZSM-5 catalyst of copper oxide compounds modified with zeolite of a silica concentration of 1.5% in mass. This system is an interesting system and is distinguished by a high stability in the NO reduction process. It possesses moreover, a high mechanical resistance with a distinct advantage of easy preparation.

MATERIALS AND METHODS

The catalytic reduction of nitrogen monoxide was studied in the laboratory using a quartz reactor (20 mm wide and 180 mm long). Analysis of raw material and reaction products was done with an LXM-8MD chromatograph equipped with a heat conductivity detector. Two chromatographic columns were used for the analysis. The first one (3 mm wide and 1 m long) used in the analysis of O₂, N₂, NO and CO was filled with CaA zeolite (0.25-0.5 mm fraction). Activation of the adsorbents was done at temperatures of 400 to 450°C for 4 hours in the open (air) and then in a helium bath for one hour at 250°C. The second column (3 mm wide and 2 m long) used in the analysis of N₂O, NO₂ and CO₂ was, on the other hand, filled with activated SKT charcoal (0.25-0.5 mm fraction). Activation of the adsorbents was done at 250°C for 5 hours in the open (air) and then in a helium bath for 3 hours at the same temperature. The two columns were thermostatically

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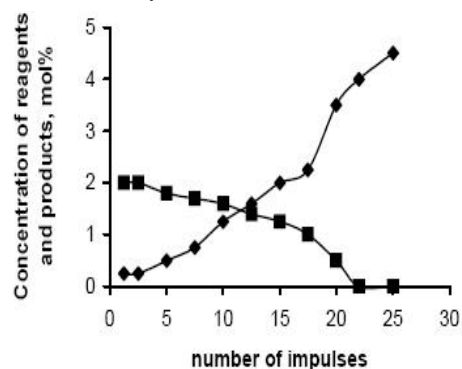


Figure 2 : Concentration of reagents and products of the reaction of NO with the CuZSM-5 catalyst relative to the number of impulses. 1 g CuZSM-5 ; temperature = 500°C ; NO concentration = 4.45 mol % ; sample heated beforehand in a 500°C air current for 5 hours

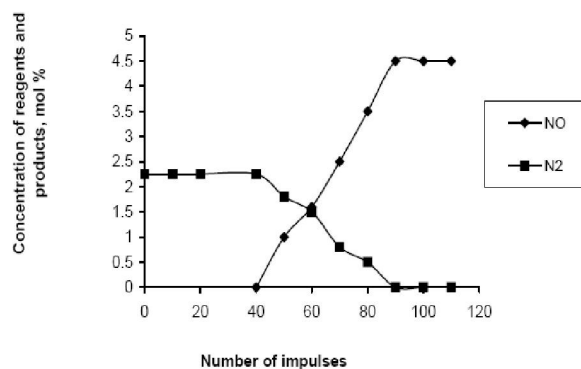


Figure 3 : Concentration of reagents and products of the reaction of NO with the CuZSM-5 catalyst relative to the number of impulses. 1 g CuZSM-5 ; temperature = 500 °C ; concentration of NO = 4.45 mol % ; sample heated before hand in a helium current heated at 500°C for 5 hours

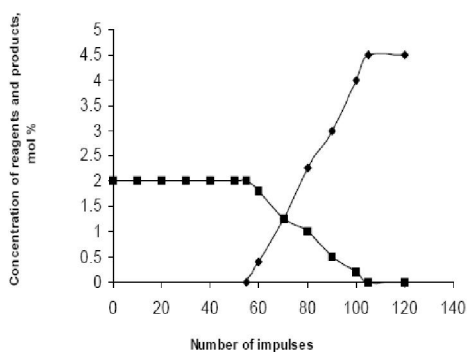


Figure 4 : Concentration of reagents and products of the reaction of NO with the CuZSM-5 relative to the number of impulses. 1 g CuZSM-5 ; temperature = 500°C ; NO concentration = 4.45 mol % ; sample heated before hand in a helium air current at 500°C for 5 hours

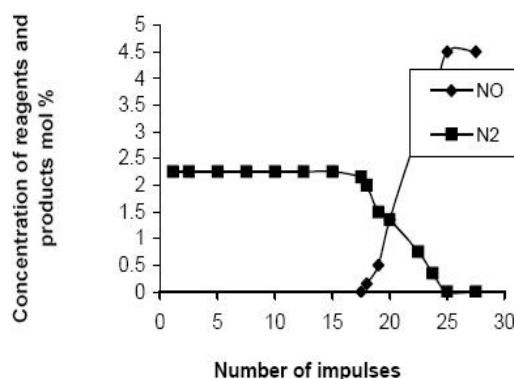


Figure 5 : Concentration of reagents and products of the reaction of NO with CO relative to the number of impulses. 0.3 g CuZSM-5 ; temperature = 700°C ; NO concentration = 4.45 mol %

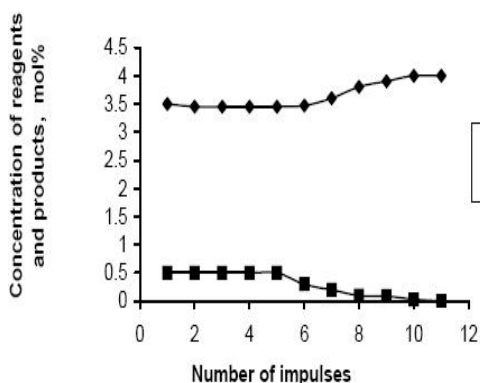


Figure 6 : Concentration of reagents and products of the reaction of NO with Cu relative to the number of impulses. 1.0 g of Cu ; temperature = 400°C ; NO concentration = 4.45 mol %

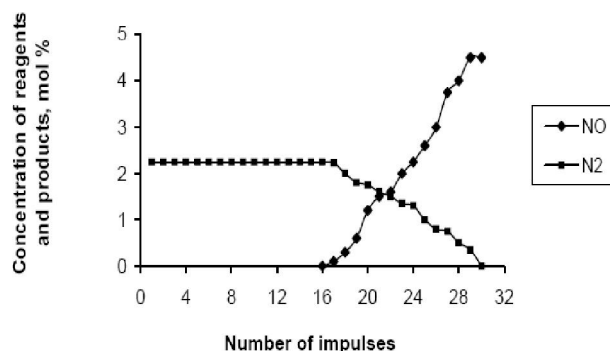


Figure 7 : Concentration of reagents and products of the reaction of NO with 1.0 % CuO/ γ -Al₂O₃ in relation to the number of impulses; 0.40 g of CuO/ γ -Al₂O₃ ; temperature = 300°C ; concentration of NO = 4.45 mol %

fixed at 70°C. The speed of the gas vector (He) in the two columns was 50 m³.min⁻¹. Sensitivity of the analysis was 0.01 mol %. The catalyst synthesis method was

that described by Alhazov and Gazan-Zade^[9] and Soualah et al.^[10]. X-ray Diffraction (XRD) was conducted on the Bruker model D8 Advance instrument

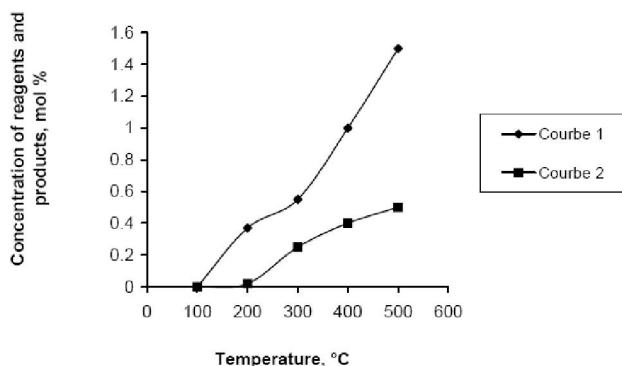


Figure 8 : Speed of the catalytic reduction of NO by CO with the catalysts; curve1: CuZSM-5; curve 2 : CuO/ γ -Al₂O₃

(operation mode, -40 kV, 30 mA, CuK _{α} , λ_{α} = 0,15406). Infrared spectroscopy of the catalyst was done with a UR-20 spectro-photometer in the 1300-3300 cm⁻¹ wave length range.

RESULTS AND DISCUSSION

The physical/chemical study of the catalyst

The study was done with CuZSM-5 catalyst of copper oxide compounds modified with zeolite of a silica concentration of 1.5% in mass. To prepare the catalyst, the ZSM-5 sodaic form was used. The SiO₂/Al₂O₃ relation was 66 in the zeolite. This zeolite possessed a monoclinical structure^[11,12]. The CuO concentration in the sample was 1% in mass. In the dehydration and reduction process, it was noticed that H₂O was completely eliminated. The specific surface of the catalyst was equal to 37 m²/g. The diffractogram of the CuZSM-5 (Figure 1) suggested that the structure of the catalyst did not change while in the reactor.

Reaction of NO with the different zeolites

Nitrogen (NO) did not react with the undehydrated zeolite sample at a temperature of 500°C. TABLE 1 gives the result of the study of this reaction with dehydrated copper compounds zeolites. It can be seen from this table that at 500°C, with 0.75% CuM and 1.5% CuM, no reaction took place. With CuZSM-5 zeolite and at a temperature of 440°C, N₂ was formed in the reaction products. The concentration of N₂ diminished from impulse to impulse, from 0.40 to 0 mol. In this case, oxygen did not form. The balance for nitrogen indicated the total absence of other secondary reactions.

TABLE 2 : Concentration of reagents and products of the reaction of NO with the CuO/ γ -Al₂O₃ catalyst at the exit of the reactor (mol %); 2.0 g CuO/ γ -Al₂O₃; Impulse concentration: NO = 4.45 mol %

Concentration of CuO in the catalyst, mol %	Reagents and products	Temperature, °C		
		300	400	500
0.5	NO	3.95	3.70	
	N ₂	0.25	0.35	
	O ₂	0	0	
1.0	NO	3.85	3.70	
	N ₂	0,30	0.35	
	O ₂	0	0	
1.5	NO	4.00	3.95	3.75
	N ₂	0.20	0.25	0.35
	O ₂	0	0	0

Increasing the temperature to 500°C, the reaction speed increased. The quantity of N₂ formed in the first four impulses was 2 mol (Figure 2). As from the fifth impulse, there was a drop in the consumption of NO and in the quantity of N₂ formed.

At the 22nd impulse NO was not consumed and N₂ did not form. There was lack of oxygen in the gaseous phase, indicating that N₂ is not the product of the decomposition of NO but that of the re-oxidation of NO reduced on the surface of the zeolites. The total amount of oxygen consumed for re-oxidation of the zeolites in the impulses was 30 mols per gram of zeolite (30 mols/g).

The re-oxidation speed of the CuZSM-5 sample, preheated in a helium (He) current, was more than the speed of re-oxidation after a preliminary heating in an air current. It can be seen from figure 3 that at t = 500°C, the total transformation of NO into N₂ with this sample was obtained at the 40th impulse.

As from the 41st impulse, the consumption of NO and formation of N₂ dropped, and touched the zero point at the 70th impulse. After that point NO was no longer consumed and N₂ was no longer formed. The consumption of oxygen at re-oxidation, from the 1st to 69th impulse, was 145 mols/g.

If the CuZSM-5 sample is heated in preparation in an air current for 5 hours and then at the same temperature in a helium current for 5 hours, its capacity of re-oxidation with NO is enhanced. In this case NO is completely transformed into N₂ at the 56th impulse. The

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TABLE 3 : Concentration of reagents and products of the reaction of NO with CO at the exit of the reactor. 1 g of zeolite; impulse volume = 0.1 cm³; concentration in the impulse: NO = 2.22 mol %; CO = 2.23 mol%

Type of zeolite	Reagents and products	Temperature °C						
		100-300	350	400	500	600	100-250	300
0.75% CuM	NO							2.22
	CO							2.23
	N ₂							0
	N ₂ O							0
	CO ₂							0
1.5% CuM	NO	2.22	1.52	1.62	1.22	1.22		
	CO	2.23	1.63	1.63	1.23	1.23		
	N ₂	0	0.25	0.30	0.50	0.50		
	N ₂ O	0	0.10	0	0	0		
	CO ₂	0	0.6	0.60	1.00	1.00		
2.2% CuM	NO		1.02	0.22	0		2.22	1.82
	CO		1.03	0.23	0		2.23	1.83
	N ₂		0.60	1.00	1.11		0	0.20
	N ₂ O		0	0	0		0	0
	CO ₂		1.20	2.00	2.23		0	0.40

TABLE 4 : Concentration of reagents and products of the reaction NO with CO at the exit of the reactor (mol %). Impulse volume = 0.1 cm³; concentration in the impulse: NO = 2.22 mol %; CO = 2.23 mol %; 1 g CuZSM-5

Reagents and products	Temperature, °C						
	100	150	200	250	300	400	500
NO	1.72	1.42	1.22	1.02	0.72	0.22	0
CO	1.73	1.43	1.23	1.03	0.73	0.23	0
N ₂	0.25	0.40	0.50	0.60	0.75	1.00	1.11
N ₂ O	0	0	0	0	0	0	0
CO ₂	0.50	0.80	1.00	1.20	1.50	2.00	2.23

reaction ends at the 105th impulse (Figure 4).

The reoxidation of NO with CuZSM-5 can be observed at a much lower temperature. CO was used as reducer. The highest amount of oxygen that could be eliminated from the CuZSM-5 with the assistance of CO, at temperatures ranging from 300 to 700°C, lay between 160 and 170 mol/g. Fig.5 gives the result of the reaction of NO with 0.3g of the CuZSM-5 sample where 49.5 mol of oxygen atoms are eliminated at 700°C.

Reaction of NO with Cu and CuO/ γ -Al₂O₃

The reaction of NO with Cu and CuO coated with

TABLE 5 : Concentration of the reagents and products of the reaction of NO with CO at the exit of the reactor (mol %). Impulse volume = 0.1 cm³; concentration in the impulse: NO = 2.22 mol %; CO = 2.23 mol %; 1 g CuO

Reagents and products	Temperature, °C				
	100	150	200	250	300-500
NO	1.22	0.82	0.92	1.02	1.02
CO	0	0.23	0	0	0
N ₂	0.50	0.60	0.65	0.60	0.60
N ₂ O	<0.1	0.10	0	0	0
CO ₂	2.23	2.00	2.13	2.23	2.23

TABLE 6 : Concentration of reagents and products of the NO reaction with CO at the exit of the reactor (mol %). Impulse volume = 0.1 cm³; concentration in the impulse: NO = 2.22 mol %; CO = 2.23 mol %; 2 g CuO/ γ -Al₂O₃

Concentration of CuO in the catalyst, mol %	Reagents and products	Temperature, °C					
		200	250	300	350	400	500
0.5	NO	2.10	1.98	1.58	1.52	1.42	1.22
	CO	2.08	1.88	1.53	1.23	1.03	0.83
	N ₂	0.05	0.10	0.25	0.30	0.40	0.50
	N ₂ O	<0.01	0.02	0.07	0.05	0	0
	CO ₂	0.15	0.35	0.70	1.00	1.20	1.40
1.0	NO	1.97	0.82		1.32	1.02	
	CO	1.93	1.73		1.23	0.73	
	N ₂	0.10	0.20		0.45	0.60	
	N ₂ O	0.03	0		0	0	
	CO ₂	0.30	0.50		1.00	1.50	
1.5	NO	1.92	1.72		1.22	0.72	
	CO	1.93	1.53		0.73	0.23	
	N ₂	0.10	0.25		0.50	0.75	
	N ₂ O	0.05	0		0	0	
	CO ₂	0.30	0.70		1.50	2.00	

γ -Al₂O₃ was studied. Copper oxide was obtained by the thermal dissociation of copper nitrate and then heated at 500°C for 4 hours. The coated catalyst was prepared according to the method described by Mehandjiev et al.^[13]. Figure 6 shows the result of the reaction of NO with CuO at t = 400°C. In the first five impulses the consumption of NO was 1 mol. To the quantity of NO in each impulse corresponded a formation of 0.5 mol of N₂. As from the fifth impulse, the speed of transformation of NO into N₂ dropped. At the tenth impulse, NO was not consumed and N₂ did not form. Oxygen was not detected in this reaction. The quantity of oxygen consumed by NO at re-oxida-

tion was 3.5 mol of atom for 1 g of CuO. TABLE 2 gives the result of the reaction of NO with the CuO/ γ -Al₂O₃. At temperatures ranging from 300 to 500°C, in all the cases, the consumption of NO and formation of N₂ was noticed.

Oxygen was not equally detected in this reaction. The increase in the concentration of Cu in the sample had absolutely no effect on the results of the five impulses. The increase in temperature from 300 to 500°C very slightly influenced the output of N₂. Figure 7 gives the result of the reaction of NO with the 1% CuO/ γ -Al₂O₃.

It stands out from this figure that for the 16 impulses of N₂ (2.25 mols) was observed at the exit of the reactor. From the 17th impulse, the speed of formation of N₂ dropped. In the reaction mixture, there was NO that did not react and its quantity increased from impulse to impulse. At the 30th impulse the speed of formation of N₂ was zero. The total consumption of oxygen at re-oxidation was 48 mols.

Reaction of NO with CO

TABLE 3 presents the result of the reaction of NO and CO. With 0.75 % CuM and at a temperature of 500°C, the reaction did not take place. The reduction of NO was observed with 1.5 % CuM at t=350°C. Products of the reaction of the reduction of NO at this temperature were N₂ and N₂O. At t ≥ 400°C, the product of the reaction was N₂. The reaction was: 2NO + 2CO → N₂ + CO₂. At a temperature of 600°C, the reduction of the catalyst with CO did not take place.

The most active of the mordenite catalysts was the 2.2% CuM sample. With this catalyst, NO reduced to N₂. Total transformation was attained at t = 500°C. The most active zeolite among all those that were studied was CuZSM-5. With a temperature of 150°C, the NO conversion rate was 36%. The CO was consumed at all temperatures of the experiment. The product of the reaction was N₂. Table 4 gives the result obtained with the CuZSM-5 catalyst.

The reduction of NO and CO was equally studied with CuO and CuO/ γ -Al₂O₃ compounds. Table 5 shows the result obtained with CuO. It can be seen from this table that at t = 100°C, CO was totally consumed in the reaction and the products obtained were N₂ and N₂O. At t = 200°C, N₂O did not form. The

reduction of CuO was observed at all temperatures of the experiment.

With the increase in temperature from 200 to 250°C the speed of reduction of NO dropped. After that, an increase in temperature to 500°C did not cause any increase in the reaction speed.

TABLE 6 gives the result obtained with the CuO/ γ -Al₂O₃ catalyst. Increasing the concentration of CuO in the catalyst from 0.5 to 1.5 % in mass increased its activity.

CONCLUSION

The use of copper oxides as catalysts in the reduction of nitrogen oxides has long retained the attention of researchers. This is due mainly to the great transformation speed of nitrogen oxides at relatively low temperatures. Figure 8 presents the compared results of the nitrogen monoxide (NO) catalytic reduction reaction speeds with the CuZSM-5 and CuO/ γ -Al₂O₃.

From this figure, it can be noticed that the speed of the NO reduction reaction by the CuZSM-5 catalyst was more than that of the NO reduction reaction by CuO/ γ -Al₂O₃. The reaction of the Cu^oZSM-5 compound, at a temperature range of 300 to 500°C, resulted in disproportionality in NO, which was accompanied by the oxidation of Cu^o to Cu²⁺. In zeolite, the Cu²⁺ ions possess a high reaction potential and are situated in the zeolite cavities. During the dehydration and reduction processes, these ions migrate to the surface of the zeolite. The CuO/ γ -Al₂O₃ catalyst is not stable under the chosen conditions and is intensely reduced by CO (TABLE 6). Among the modified mordenite compounds zeolite copper oxides systems, 0.75% CuM, 1.5% CuM, 2.2% CuM and CuZSM-5, the most active in NO reduction is the CuZSM-5 catalyst.

By comparing the catalytic activity of CuZSM-5 and the unmodified CuO/ γ -Al₂O₃, it can be said that the most active is the CuZSM-5 catalyst modified with zeolite at a concentration in silica of 1.5% in mass. The advantages of these catalysts are seen in a good catalytic activity in the nitrogen monoxide reduction process and by their high stability under the reaction conditions.

This catalyst can safely be recommended for use in the purification of nitrogen monoxide emissions.

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