

## The Cu-ZSM-5 Catalysts Washcoated on Monolith for Diesel Vehicle Emission Control

S. A. YASHNIK<sup>1</sup>, L. T. TSYKOZA<sup>1</sup>, Z. R. ISMAGILOV<sup>1</sup>, V. A. SAZONOV<sup>1</sup>, N. V. SHIKINA<sup>1</sup>, V. V. KUZNETSOV<sup>1</sup>, I. A. OVSYANNIKOVA<sup>1</sup>, N. M. DANCHENKO<sup>2</sup>, S. P. DENISOV<sup>2</sup> and H. J. VERINGA<sup>3</sup>

<sup>1</sup>G. K. Borekov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 5, Novosibirsk 630090 (Russia)

E-mail: ZRI@catalysis.nsk.su

<sup>2</sup>Ural Electrochemical Plant, Novoural'sk (Russia)

<sup>3</sup>ECN, Westerduinweg 3, 1755 ZG Petten (The Netherlands)

### Abstract

The composition of modified monolith zeolite catalysts containing the basic components in the washcoating layer is suggested. When the washcoating layer contains 80 % zeolite, 10 % TiO<sub>2</sub>, and 10 % Al<sub>2</sub>O<sub>3</sub>, the catalyst exhibits both activity and adhesion strength. The titanium catalyst is stable to sulfur poisoning (H<sub>2</sub>S) at 500 °C; a small decrease in the catalyst activity at 400 °C is no longer observed after regeneration. Introducing 4 % mass Ce (calculated for respect to the washcoating) into the ready catalyst, one can preserve the catalyst activity and provide its stable operation in the presence of water vapor both at 400 and 500 °C. Activity of the titanium-cerium-modified monolith catalyst is stable in the presence of water vapor and sulfur compounds in the gas mixture at a time.

### INTRODUCTION

Data on the preparation and investigation of bulk Cu-ZSM-5 catalysts [1, 2] permitted us to choose the optimal ion exchange conditions, providing both high activity and stability of the catalysts. In the present work we use our earlier data [1, 2] to synthesize and study the monolith catalysts containing copper-substituted zeolites in the washcoating and their operation on the selective catalytic reduction of nitrogen oxides (SCR NO<sub>x</sub>) with propane in the presence of water vapor and sulfur compounds.

As is known, the Cu-substituted zeolites exhibit high activity on SCR NO<sub>x</sub> with hydrocarbons and lose their activity in excess of oxygen [3–5], water vapor and/or SO<sub>2</sub> [3, 6]. The catalyst activity can be partially reduced by regeneration, the degree of regeneration depends on the concentration of poisons in the reaction mixture. Thus, when the concentration of water is low (2 % vol. [6] or 3.9 % vol. [3] for 90 min [3]), the catalyst deactivation is

a reversible process and the catalyst activity is completely reduced by regeneration. A treatment of the zeolite catalyst in wet air (to 14 % vol. water) in a temperature range of 200–600 °C [7, 8] results in a sharp decay in the Cu-ZSM-5 activity. A partial reduction of the activity after regeneration was attributed to [7, 8] dealuminizing of the zeolite.

When waste gas contains sulfur compounds (SO<sub>2</sub> concentration is to 20 ppm) and the degree of NO conversion is high, the activity of Cu-ZSM-5 catalysts slightly decreases on SCR NO<sub>x</sub> with hydrocarbons. The catalyst activity is completely restored by termination of SO<sub>2</sub> feeding into the reaction mixture [3, 9]. Because of the presence of SO<sub>2</sub> (220–300 ppm) in the gas mixture, Cu-ZSM-5 partially loses its activity on SCR NO<sub>x</sub> with hydrocarbons [3, 10] and becomes completely deactivated in the reaction of direct NO<sub>x</sub> decomposition [10]. In the latter case, the activity of Cu-ZSM-5 is partially restored after its training in a helium flow at 700 °C.

When the reaction of SCR  $\text{NO}_x$  with hydrocarbons is promoted oxygen (the concentration of oxygen in the reaction mixture is 10 % vol.), the activity of Cu-ZSM-5 is 60 times higher than in the absence of oxygen [4]. On the other hand, the dependence of activity of Cu-substituted zeolites on the oxygen concentration in the reaction mixture is maximum at oxygen concentrations ranging from 2 to 3 % vol., the degree of conversion slowly decreases as the concentration of oxygen rises. Interestingly, oxygen-containing hydrocarbons can restore NO under highly oxidizing conditions [5].

Though zeolite catalysts have high initial activity, their application in the actual purification processes as cleaning of vehicle waste gases is limited because of their susceptibility to deactivation in the presence of water vapor and sulfur.

The number of publications devoted to the improvement of catalysts for the selective reduction of  $\text{NO}_x$  in the presence of  $\text{SO}_2$  and water vapor is not large. It is well known that the catalytic systems containing titanium, cerium and aluminum oxides are more stable to poisoning with water vapor and sulfur compounds during the SCR  $\text{NO}_x$  with ammonia. On studying the stability of copper and/or vanadium oxides supported on the alumina and titania or their mixture on the SCR  $\text{NO}_x$  with ammonia in the presence of  $\text{SO}_2$  [11], it was shown that catalysts based on  $\text{TiO}_2$  are more stable to sulfur poisoning. Note that as the concentration of  $\text{TiO}_2$  in the support increases, the catalyst activity holds at a higher level. In addition, the resistance of vanadium catalysts to sulfur poisoning increases if a support contains both  $\text{TiO}_2$  and ~20 %  $\text{Al}_2\text{O}_3$ . A comparison of the copper and/or vanadium

oxides supported on the same carrier shows that the copper catalyst is less stable to  $\text{SO}_2$  poisoning, though it effectively removes  $\text{SO}_2$  as a sorbent/catalyst. The authors attribute the loss of stability of the copper catalyst to its high capacity with respect to  $\text{SO}_2$  and to formation of complex copper-aluminum sulfates. Studying the selective reduction of NO with decane on Cu-ZSM-5,  $\text{CuO}/\text{Al}_2\text{O}_3$ ,  $\text{CuO}/\text{ZrO}_2$ , and  $\text{CuO}/\text{TiO}_2$  in the presence of  $\text{SO}_2$  [12], the authors attributed a lesser decrease in the activity of the latter two systems to the presence of strong Lewis sites in both catalysts.

According to refs. [13, 14], the  $\text{CuO}/\text{TiO}_2$  catalysts, pre-sulfated in gas mixture  $\text{SO}_2 + \text{O}_2$  at temperatures above 400 °C or prepared from copper sulfate [13–15] are highly active in the reaction of SCR  $\text{NO}_x$  with ammonia and stable with respect to  $\text{SO}_2$ . Activity of Cu–Ti–O catalysts in the reaction is primarily determined by redox properties of copper. An introduction of sulfate ions into the Cu–Ti–O systems hinders the reduction of Cu(II) [12, 15, 16] and increases the activity of the system at temperatures above 400 °C because of sulfation of titania and formation of copper sulfate [15].

Modifying the copper-substituted zeolite catalyst with cations as Cr, Ce or Sr [17, 18], one increases their thermal and hydrothermal stability in the presence of water vapor and  $\text{SO}_2$ . This phenomenon is probably caused by prevention or inhibition of the processes of sintering of the active copper-containing structures in the zeolite and dealumination of the zeolite itself.

Based on the few reference data, in our work the monolith catalysts were prepared using titania and cerium oxide as modifying agents

TABLE 1

Properties of monolith supports

Support	Channel size, mm	Wall thickness, mm	Phase composition	$S_{sp}$ , $\text{m}^2/\text{g}$	Pore volume (with respect to water), $\text{cm}^3/\text{g}$
Alumosilicate	2.2×2.2	0.45	$\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$	0.45	0.20
Cordierite	1.0×1.0	0.10	$\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$	0.30	0.12

in order to increase their resistance to water and sulfur poisoning.

## EXPERIMENTAL

Alumosilicate or cordierite monolith fragments (10×10×20 mm in size) were used as monolith supports (Table 1).

The samples of H-ZSM-5 zeolite [1, 2, 19] were used to prepare the catalysts, the zeolite module (atomic ratio Si/Al) was 34 and 73. The washcoated monolith catalysts were synthesized via the below steps:

- preparation of a suspension, containing 80 % zeolite and 20 % binding agent (calculated for Al<sub>2</sub>O<sub>3</sub>) from aluminum hydroxide with a pseudoboehmite structure as in ref. [2, 19];

- deposition of a washcoat on the monolith support by its submerging into the suspension, drying and heating at 550 °C;

- performance of ion exchange from solutions of copper acetate (pH ~ 6) or ammonia copper acetate (pH ~ 10), the concentration of copper is 5–10 mg/ml [1, 2]. Then the washcoated monolith catalyst is washed, dried and calcined at 500 °C.

For titania modifying, we introduced a disperse powder of 10 % TiO<sub>2</sub> (anatase modification) instead of 10 % Al<sub>2</sub>O<sub>3</sub> at the step of suspension preparation. The prepared catalyst was modified with cerium oxide via incipient wetness technique the given concentration of cerium (2 and 4 % mass) in the coating. Then the catalyst was dried and calcined at 500 °C.

As in earlier works [1, 2], activity of the modified catalysts was tested on the NO reduction with propane, the space velocity of gas flow was 42 000 h<sup>-1</sup>, temperature ranged from 200 to 500 °C, the gas mixture had the following composition: NO 300 ppm, C<sub>3</sub>H<sub>8</sub> 0.15 % vol., O<sub>2</sub> 3.5 % vol., N<sub>2</sub> balance. Activity of the catalysts at standard conditions was characterized by the degree of NO conversion ( $X_o$ , %) at the preset temperature.

After determination of NO conversion ( $X_o$ ) at standard conditions, we introduced hydrogen sulfide (~300 ppm) and/or water vapor (~6 % vol.) into the reaction mixture at the preset temperature (400 or 500 °C). The cata-

lysts were poisoned with the above admixtures during 30 min (one cycle), then the feeding of H<sub>2</sub>S and/or water vapor was stopped and the degree of NO conversion was determined in the standard reaction mixture ( $X_k$ , %) at the same temperature. Stability of the catalysts to poisoning with sulfur and water vapor was determined from parameter  $\Delta X/X_o$  (determined as  $(X_o - X_k)/X_o$  and expressed in %).

To determine stability of the catalysts in the presence of hydrogen sulfide and/or water vapor, poisoning lasted for 20 h, activity was measured every 2–4 h at standard conditions. The catalysts were regenerated at 500 °C for 0.5–2 h in a flow of air. Activity was determined after regeneration of catalysts at standard conditions ( $X_{reg}$ , %).

In order to study the effect of concentration of oxygen and NO on the catalyst activity, the concentration of O<sub>2</sub> varied from 3 to 12 % vol. and of NO from 300 to 900 ppm. Studies were performed on the cordierite based monolith catalysts with an optimal composition of the zeolite coating.

The catalysts were subjected to DIESEL tests at the Electrochemical Plant (Novouralsk, Russia), the space velocity was 50 000 h<sup>-1</sup>, the temperature was 400 °C, and the gas mixture contained: O<sub>2</sub> 14.5 % vol., NO 300 ppm, CO 1900 ppm, C<sub>3</sub>H<sub>6</sub> 200 ppm, C<sub>3</sub>H<sub>8</sub> 300 ppm, CO<sub>2</sub> 2500 ppm, H<sub>2</sub>O 2.5 % vol., nitrogen being the balance. Testing was performed on the cordierite based monoliths 25 mm in diameter and 75 mm in length, the composition of the zeolite-containing washcoat was optimal.

Morphology of the catalysts was characterized using the scanning electron microscopy method on a REM-100U electron microscope.

XRD was performed using a HZG-4 diffractometer supplied with CuK<sub>α</sub> radiation. Phase composition was determined from diffraction patterns registered at 1°/min and 2θ = 4–40°.

Formation of sulfur compounds on the catalyst surface subjected to poisoning with hydrogen sulfide was studied using a MAP-3 micro-analyzer. The probe diameter was 1–2 mm, the working voltage was 25 kW, K<sub>α</sub>Al, K<sub>β</sub>Ti, K<sub>α</sub>Cu, and K<sub>α</sub>S were analytical lines.

## RESULTS AND DISCUSSION

### Initial activity of the monolith catalysts

In this work we studied the monolith catalysts whose washcoating have the below compositions: (1) Cu [80 % ZSM-5 + 20 %  $\text{Al}_2\text{O}_3$ ], (2) Cu [80 % ZSM-5 + 10 %  $\text{TiO}_2$  + 10 %  $\text{Al}_2\text{O}_3$ ], (3) Ce{Cu[80 % ZSM-5 + 20 %  $\text{Al}_2\text{O}_3$ ]}, (4) Ce{Cu[80 % ZSM-5 + 10 %  $\text{TiO}_2$  + 10 %  $\text{Al}_2\text{O}_3$ ]}.

In all synthesized monolith catalysts, the washcoat was 10–13 % mass. The concentration of both copper and cerium in the washcoating was 1–4 % mass. According to the scanning electron microscopy (Fig. 1), the support surface is densely covered with a homogeneous (without defects) washcoating layer. To provide uniform and strong coverage of cordierite and aluminosilicate based supports, the optimal thickness of the washcoat should be 15–20 and 20–50  $\mu\text{m}$ , respectively.

Table 2 presents data on the activity of monolith catalysts with a zeolite washcoat, the supports have different geometries, the experimental conditions are standard (without poisoning admixtures). For comparison, the table presents the activity of bulk Cu-ZSM-5 catalysts [1] which differ by copper concentration (1.1 and 3.5 % mass) and zeolite module ( $\text{Si}/\text{Al} = 34$  and 73). It was shown [1] that irrespective of the zeolite module, the activity of bulk Cu-ZSM-5 catalysts reaches its maximum (the absolute maximal activity is 94–97 % at  $T = 400$ – $500$  °C) when the level of ion exchange ( $2 \times 100 \times \text{Cu}/\text{Al}$ , % [20]) is close to 100 %.

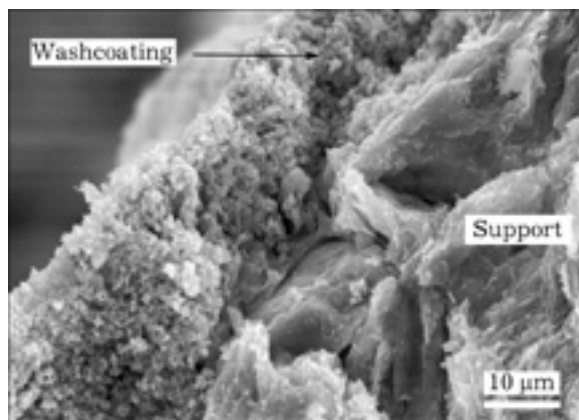


Fig. 1. Micrographs of surface of the washcoated support.

This maximum activity maintains as the degree of exchange increases to 430 %. According to [2], an introduction of 20 % mass  $\text{Al}_2\text{O}_3$  or 10 % mass  $\text{TiO}_2$  + 10 % mass  $\text{Al}_2\text{O}_3$  results in a small decrease in the activity of the bulk zeolite-containing composition.

At 400 °C, the activity of the monolith catalysts with a washcoating supported on the aluminosilicate or cordierite is 30–47 % rel. lower than that of the bulk catalysts of similar composition (compare samples 3 and 7, 12; 5 and 9, 13; 6 and 8 in Table 2). The difference between activity of the bulk and washcoat monolith catalysts reduces to 17–24 % rel. as temperature rises to 500 °C.

When the conditions of ion exchange provide the exchange degree close to 100 % (the concentration of copper acetate solution is not lower than 5 mg CuO/ml [1, 2]), the zeolite module does not affect the activity of monolith catalysts based aluminosilicate (compare samples No. 10 and 11 in Table 2) as in the case of bulk Cu-ZSM-5 catalysts [1]. In case of the catalysts containing copper-substituted zeolite and 20 %  $\text{Al}_2\text{O}_3$  in the washcoat, introduction of 10 %  $\text{TiO}_2$  instead of 10 %  $\text{Al}_2\text{O}_3$  into the washcoat does not change the catalysts activity (compare samples No. 12 and 13).

As cerium dioxide is introduced in the washcoated monolith catalysts, the activity decreases (compare samples No. 4 and 6, 9 and 10, 13, 14, and 15 in Table 2). When the concentration of cerium dioxide is 2–4 % mass, the activity decreases by 40–60 % rel. at 300–400 °C and by 10–20 % rel. at 450–500 °C. It should be noted that an introduction of both 2 and 4 % mass  $\text{CeO}_2$  changes less the activity of catalysts prepared by ion exchange from solutions containing 5 mg CuO/ml that those prepared from the solutions containing 10 mg CuO/ml.

For comparison, Table 2 presents literary data on the activity of monolith catalysts with a washcoat containing Co or (Co-Cu)-substituted zeolite [21]. Taking into account the fact that nitrogen oxide was reduced with ethylene [21] and the time of contact was 3.5 times longer than in our work, one can conclude that the activity of the samples is comparable.

As the concentration of NO in the reaction mixture is raised from 300 to 900 ppm and the concentrations of  $\text{C}_3\text{H}_8$  and  $\text{O}_2$  are ~ 1200 ppm

TABLE 2

Properties of the synthesized bulk and washcoat monolith catalysts

No.	Washcoat composition	NO conversion, %, at T, °C		
		400	450	500
1	3.5 % Cu-ZSM-5 (bulk), Si/Al = 73, [1]	94	99	97
2	1.1 % Cu-ZSM-5 (bulk), Si/Al = 34, [1]	94	97	96
3	0.9 % Cu[80 % ZSM-5 + 20 % Al <sub>2</sub> O <sub>3</sub> ] (bulk), Si/Al = 73, [2]	85	92	93
4	0.9 % Cu[80 % ZSM-5 + 20 % Al <sub>2</sub> O <sub>3</sub> ] (bulk), Si/Al = 34, [2]	77	86	90
5	1.6 % Cu[80 % ZSM-5 + 10 % TiO <sub>2</sub> +10 % Al <sub>2</sub> O <sub>3</sub> ] (bulk), Si/Al=34, [19]	84	87	87
6	4 % Ce{1.2 % Cu[80 % ZSM-5 + 20 % Al <sub>2</sub> O <sub>3</sub> ]} (bulk), Si/Al = 34, [19]	64	77	84
7	Cu[80 % ZSM-5 + 20 % Al <sub>2</sub> O <sub>3</sub> ]/alumosilicate, Si/Al = 73, [19]	45	65	70
8	Ce{Cu[80 % ZSM-5 + 20 % Al <sub>2</sub> O <sub>3</sub> ]} /alumosilicate, Si/Al = 73, [19]	43	62	69
9	Cu[80 % ZSM-5 + 10 % TiO <sub>2</sub> + 10 % Al <sub>2</sub> O <sub>3</sub> ]/alumosilicate, Si/Al=34, [19]	55	64	72
10	4 % Ce{Cu[80 % ZSM-5 + 10 % TiO <sub>2</sub> + 10 % Al <sub>2</sub> O <sub>3</sub> ]} /alumosilicate, Si/Al = 34, [19]	48	60	64
11	4 % Ce{Cu[80 % ZSM-5 + 10 % TiO <sub>2</sub> + 10 % Al <sub>2</sub> O <sub>3</sub> ]} /alumosilicate, Si/Al = 73, [19]	48	59	65
12	Cu[80 % ZSM-5 + 20 % Al <sub>2</sub> O <sub>3</sub> ]/cordierite, Si/Al = 34	60	70	73
13	Cu[80 % ZSM-5 + 10 % TiO <sub>2</sub> + 10 % Al <sub>2</sub> O <sub>3</sub> ]/cordierite, Si/Al=34	58	67	72
14	2 % Ce{Cu[80 % ZSM-5 + 10 % TiO <sub>2</sub> + 10 % Al <sub>2</sub> O <sub>3</sub> ]} /cordierite, Si/Al = 34	45	59	64
15	4 % Ce{Cu[80 % ZSM-5 + 10 % TiO <sub>2</sub> + 10 % Al <sub>2</sub> O <sub>3</sub> ]} /cordierite, Si/Al = 34	37	56	61
16	Co-ZSM-5, [21]*	89	96	95
17	[Cu-ZSM-5 + Co-ZSM-5], [21]*	89	90	89

\*The space velocity is 12 000 h<sup>-1</sup>, C<sub>2</sub>H<sub>4</sub> is a reducing agent.

and 4.2 % vol. respectively, the degree of NO conversion on the cordierite based catalyst modified with titania and cerium oxide preserves constant and is 18–22 % at 400 °C and 39–42 % at 500 °C.

#### Activity of the monolith catalysts after poisoning with H<sub>2</sub>S and/or H<sub>2</sub>O

Actual diesel vehicle emission gases contain large amounts of oxygen (~ 5–12 % vol.), water vapor (~ 10 % vol.), and SO<sub>2</sub> (~ 20 ppm) [3, 5, 7], for this reason it is important to elucidate their effect on the activity of copper-substituted zeolite catalysts.

In our recent work [19] we have shown that H<sub>2</sub>S completely converts into SO<sub>2</sub> at temperatures higher than 250 °C on both bulk and monolith Cu-ZSM-5 catalysts. Changes in the catalyst activity (sample 9 in Table 2) and concentration of SO<sub>2</sub> at the reactor outlet were studied during one cycle of poisoning with H<sub>2</sub>S at 400 and 500 °C [19]. At the instant H<sub>2</sub>S is

introduced into the gas mixture at 400 °C, the degree of NO conversion decays rapidly and the outlet concentration of SO<sub>2</sub> increases at a time. Then both parameters become stable. As H<sub>2</sub>S feeding is cut off, the catalyst activity lightly increases at 400 °C, but the initial activity is recovered only after the catalyst regeneration. At 500 °C, the catalyst activity decreases from 65 to 60 % during H<sub>2</sub>S feeding into the gas mixture and regains its initial value as H<sub>2</sub>S supply is cut off. Note that SO<sub>2</sub> emission was not observed when the catalyst was regenerated at 550 °C.

Deactivation of the catalyst observed during one poisoning cycle at 400 and 500 °C, partial reduction of the catalyst activity after removal of H<sub>2</sub>S and SO<sub>2</sub> from the gas mixture and the possibility of almost complete catalyst regeneration at 550 °C during 30 min indicate that the interaction of SO<sub>2</sub> with the catalyst surface is of the adsorption nature. The observation that the catalyst stability to sulfur poisoning sharply increases as temperature raises

TABLE 3

Activity of monolith catalysts after one cycle of poisoning with water or/and hydrogen sulfide

No.	Washcoat composition	T, °C	NO conversion					
			X <sub>0</sub> , %	Poisoning		X <sub>k</sub> , %	ΔX/X <sub>0</sub> , %	X <sub>reg</sub> , %
				H <sub>2</sub> O	H <sub>2</sub> S			
1	Cu[80 % ZSM-5 + 20 % Al <sub>2</sub> O <sub>3</sub> ] (Sample 7, Table 2)	400	45	-	+	10	78	29
		500	70			41	44	52
2	Cu[80 % ZSM-5 + 10 % TiO <sub>2</sub> + 10 % Al <sub>2</sub> O <sub>3</sub> ] (Sample 9, Table 2)	400	56	-	+	40	29	55
		500	65			64	2	64
3	Ce{Cu[80 % ZSM-5 + 10 % TiO <sub>2</sub> + 10 % Al <sub>2</sub> O <sub>3</sub> ]}	400	42	-	+	26	38	42
		500	54			54	0	54
4	Cu[80 % ZSM-5 + 20 % Al <sub>2</sub> O <sub>3</sub> ] (Sample 7, Table 2)	400	45	+	-	8	82	42
5	Cu[80 % ZSM-5 + 10 % TiO <sub>2</sub> + 10 % Al <sub>2</sub> O <sub>3</sub> ] (Sample 9, Table 2)	400	55	+	-	10	82	53
6	Ce{Cu[80 % ZSM-5 + 10 % TiO <sub>2</sub> + 10 % Al <sub>2</sub> O <sub>3</sub> ]}	400	41	+	-	41	0	41
		500	54			54	0	54
7	Ce{Cu[80 % ZSM-5 + 10 % TiO <sub>2</sub> + 10 % Al <sub>2</sub> O <sub>3</sub> ]}	400	44	+	+	26	40	44
		500	56			56	0	56

from 300 to 500 °C also confirms the adsorption nature of SO<sub>2</sub> interaction with the catalyst surface.

In the presence of water vapor in the reaction gas mixture, the dynamics of a decrease in the activity of the above catalyst is similar.

Based on the testing results one can suggest that the degree of catalyst deactivation during poisoning with water or sulfur and consequently their stability to these poisons is determined by the catalyst composition and reaction temperature and can be estimated using ΔX/X<sub>0</sub>. Data on the catalyst stability to poisoning with water vapor and sulfur are given in Table 3.

A comparison of ΔX/X<sub>0</sub> for samples No. 1, 2, and 3 (see Table 3) shows that it is possible to increase the catalyst stability to hydrogen sulfide both at 400 and 500 °C by modifying the washcoat with titanium dioxide. Regenerating (500 °C, 30 min, air flow) the catalysts containing 10 % TiO<sub>2</sub> in the washcoat, one can completely restore their initial activity. When the catalyst sample is not doped with TiO<sub>2</sub>, its activity restores only partially.

Introduction of ~ 4 % mass cerium into the washcoat provides the catalyst stability at 400–500 °C in the presence of water vapor (compare ΔX/X<sub>0</sub> for samples 5 and 6 in Table 3).

When the catalyst modified with titania and cerium oxide (sample 10 in Table 2) is treated with water vapor and sulfur compounds, it behaves as in the case of poisoning with hydrogen sulfide alone (compare samples 3 and 7). After regeneration, the catalyst activity restores completely.

Stability of the titanium-cerium modified catalyst supported on the aluminosilicate monolith (sample 10 in Table 2) was studied during long-term tests both in the presence and in the absence of poisons at a temperature of 400 °C when maximal changes in the catalyst activity are observed during short-term poisoning of catalysts. The results are given in Table 4.

Activity of the catalyst subjected to poisoning with hydrogen sulfide for 20 h at 400 °C changes as in the case of short-term poisoning [19]. The catalyst activity decreases and ΔX/X<sub>0</sub> is 54 % rel. after 20 h of catalyst deactivation. Regeneration at 500 °C for 30 min results in a partial restoration of the catalyst activity and a four-hour regeneration recovers almost completely the initial catalyst activity. According to X-ray microanalysis (Fig. 2), about 0.8 % of sulfur compounds (compare to 1.1 % sulfur immediately after sulfur poisoning) remain in the washcoat after long regeneration and com-

TABLE 4

Activity of monolith catalysts subjected to long poisoning (20 h) with water vapor and /or hydrogen sulfide

No.	Washcoat composition	T, °C	NO conversion					
			X <sub>o</sub> , %	Poisoning		X <sub>k</sub> , %	ΔX/X <sub>o</sub> , %	X <sub>reg</sub> , %
				H <sub>2</sub> O	H <sub>2</sub> S			
1	Ce{Cu[80 % ZSM-5 + 10 % TiO <sub>2</sub> + 10 % Al <sub>2</sub> O <sub>3</sub> ]} (analogue of Sample 10, Table 2)	400	41	-	-	39	5	-
2	Ce{Cu[80 % ZSM-5 + 10 % TiO <sub>2</sub> + 10 % Al <sub>2</sub> O <sub>3</sub> ]} (analogue of Sample 10, Table 2)	400	39	+	-	27	31	36
3	Ce{Cu[80 % ZSM-5 + 10 % TiO <sub>2</sub> + 10 % Al <sub>2</sub> O <sub>3</sub> ]} (analogue of Sample 10, Table 2)	400	39	-	+	18	54	23
4	Ce{Cu[80 % ZSM-5 + 10 % TiO <sub>2</sub> + 10 % Al <sub>2</sub> O <sub>3</sub> ]} (analogue of Sample 10, Table 2)	400	37	+	+	28	24	36

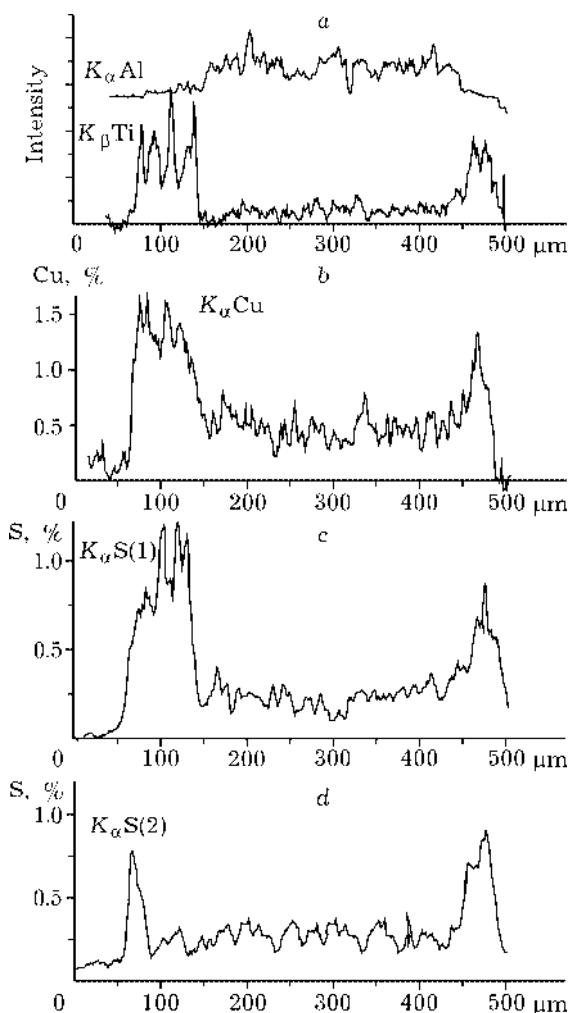


Fig. 2. Intensity of  $K_{\alpha}Al \times 2 \cdot 10^4$ ,  $K_{\beta}Ti \times 200$  (a),  $K_{\alpha}Cu \times 200$  (b),  $K_{\alpha}S(1) \times 200$  (c) lines for the washcoated catalyst after long poisoning with hydrogen sulfide and spectrum  $K_{\alpha}S(2) \times 200$  after catalyst regeneration at 500 °C for 4 h.

plete restoration of the initial catalyst activity. Since line  $K_{\alpha}S$  behaves similar to line  $K_{\alpha}Cu$  and partially follows line  $K_{\beta}Ti$ , one can suggest that sulfur is bonded with copper and titanium, but the bond with copper is more pronounced.

A testing of the catalyst (sample 10 in Table 2) in the presence of water vapor at 400 °C for 20 h results in a significant decrease in the catalyst activity (note that this decrease is not observed for a short-term poisoning of this catalyst). After regeneration at 500 °C for 30 min in air, the catalyst activity restores almost completely. A comparison of the diffraction patterns of the Cu-ZSM-5 catalyst (Si/Al = 34 and 3.1 % Cu) before and after its testing for 20 h in the presence and absence of water vapor does not reveal changes in the initial structure of Cu-ZSM-5: the diffraction patterns of the samples are similar to those of zeolite H-ZSM-5.

In the presence of both water vapor and hydrogen sulfide in the gas mixture at 400 °C for 20 h, the catalyst activity decreases by 24 % rel. and restores completely after regeneration at 500 °C for 30 min.

For the catalyst with a washcoat supported on the cordierite and promoted with both titanium and cerium oxides (sample 15 in Table 2), the dynamics of changes in the activity in the presence of water vapor and/or sulfur is similar. The catalyst loses its activity after the introduction of water vapor (~ 6 % vol.) into the

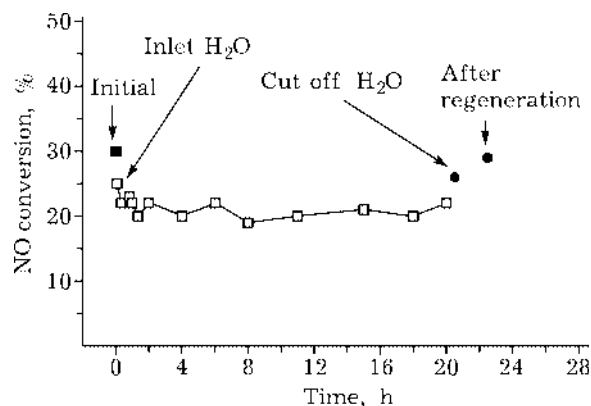


Fig. 3. Changes in the NO conversion on sample 15 (Table 2) in the presence of water vapor (6 % vol.) at 400 °C.

reaction mixture during the initial 15–20 min (Fig. 3). During the next 20 h the activity holds at a level of 20–22 %. The catalyst restores its activity after regeneration at 500 °C for 30 min.

#### *Effect of the concentration of oxygen and water vapor on the NO conversion*

As water vapor (~ 2.5 % vol.) is introduced into the reaction mixture and the concentration of oxygen is raised from 3.5 to 12 % vol. at a time, the catalyst activity significantly decreases over the entire temperature range. For the catalysts modified with titanium and cerium oxides, the maximal degree of NO conversion is 30–32 % at 500 °C, which corresponds to a two-fold dip in the catalyst activity as compared to the NO conversion in the dry mixture, containing ~ 3.5 % vol. oxygen ( $X_{\text{NO}} \sim 61\text{--}64\%$ ).

Figure 4 shows the dynamics of changes in the activity of the above catalyst in the presence of water vapor (2.5 % vol.) and at varying concentrations of oxygen in the reaction mixture. The figure suggests that the degree of NO conversion is the same at 400 °C and reaches 16–18 % when the concentration of oxygen in the dry reaction mixture is 3.5 and 12 % vol. As water vapor is introduced in the above reaction mixtures, the catalyst activity decays. When the reaction mixture contains ~3.5 % vol. O<sub>2</sub>, an introduction of water vapor decreases the catalyst activity up to 15 %. After termination of water vapor feeding into the reaction mixture, the catalyst activity re-

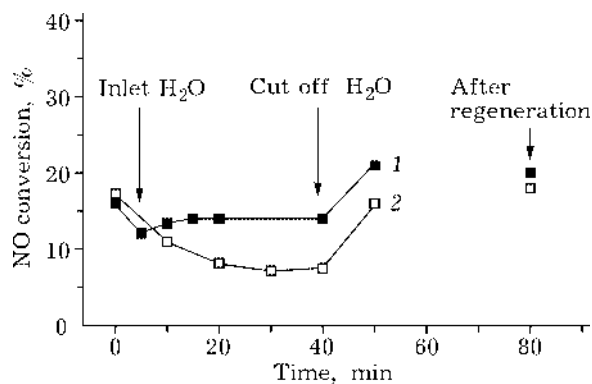


Fig. 4. Stability of sample 15 (Table 2) in the presence of water vapor (2.5 % vol.) at varying concentration of oxygen at 400 °C: 1 – 3.5 % vol. O<sub>2</sub>, 2 – 12 % vol. O<sub>2</sub>.

stores to its initial value. When water vapor is introduced into the mixture containing ~12 % vol. O<sub>2</sub>, the catalyst activity decays by a factor of 2 and restores completely after termination of water feeding and regeneration of the catalyst at 500 °C for 30 min (see Fig. 4). Therefore, the monolith catalyst with a modified Cu-ZSM-5 washcoat layer undergoes significant deactivation by small amounts of water vapor (~2.5 % vol.) in the presence of large amounts of oxygen (~12 % vol.).

#### *DIESEL tests of the catalyst modified with titanium and cerium oxide admixtures*

The cordierite based catalyst, containing 4 % Ce/1 % Cu(80 % ZSM-5 + 10 % TiO<sub>2</sub> + 10 % Al<sub>2</sub>O<sub>3</sub>) in the washcoat layer, was subjected to DIESEL tests. Three samples were aged in the moist air atmosphere during 4 h at 500, 600, and 800 °C, respectively. The catalyst preliminarily aged at 500 °C for 4 h in moist air was additionally aged at ~800 °C for 7 h in dry air. The catalyst activity was characterized by a temperature at which 50 % conversion of hydrocarbons (HC) and carbon monoxide (CO) was obtained and by the conversion of HC, CO, and NO at 400 °C. The results of testing of the fresh catalyst samples (No. 1–3) and the samples aged at different conditions are given in Table 5.

According to DIESEL test, simulating the lean-burn operation conditions, the fresh catalysts containing Cu-ZSM-5 and titanium and cerium modifying agents in the washcoat ex-



TABLE 5

DIESEL testing of the cordierite based catalyst containing 4 % Ce/1 % Cu (80 % ZSM-5 + 10 % TiO<sub>2</sub> + 10 % Al<sub>2</sub>O<sub>3</sub>) in the washcoat

Catalysts	Conversion temperature ( $T_{50}$ %), °C		Conversion at 400 °C, %		
	HC	CO	HC	CO	NO
Fresh samples					
1	323	357	70	86	8
2	318	358	71	87	9
3	321	362	71	83	10
Samples aged					
in moist air at					
500 °C/4h	330	379	70	74	9
600 °C/4h	335	393	70	63	8
800 °C/4h	–	–	16	9	3
800 °C/7h, dry air	396	–	55	16	5

hibit rather low activity. At 400 °C, the average values conversion of hydrocarbons, CO and NO are 70, 85 and 9 %, respectively. When the catalyst is aged in moist air, the conversion of CO tends to decrease as the aging temperature rises from 500 to 600 °C. Note that the catalyst aging at the above conditions does not affect its activity with respect to HC and NO. As the temperature of aging in the moist air atmosphere increases to 800 °C, the catalyst completely loses its activity, the conversion of HC, CO, and NO decreases by a factor of 4, 9 and 3, respectively. When the catalyst was preliminary aged at 500 °C in the presence of water vapor and then additionally aged at 800 °C in dry air, the catalyst activity decreases by a factor of 1.3, 5.3 and 2 with respect to HC, CO and NO, respectively. Thus, the DIESEL test suggests that the catalyst is significantly deactivated at 800 °C. Note that water vapor enlarges the degree of catalyst deactivation.

It should be noted that thermal aging at 800 °C in the atmosphere of dry gas mixtures as 5 % H<sub>2</sub>/N<sub>2</sub> and 5 % O<sub>2</sub>/N<sub>2</sub> and hydrothermal aging at 500–600 °C in the presence of water vapor (to 10 % vol.) were observed for the bulk [22, 23] and monolith [24] Cu-ZSM-5 catalysts. Thus, the activity of the monolith Cu-ZSM-5 catalyst [24] decayed from 60 to 17 % during 70 h at 485 °C in the reaction mixture simulating the lean-burn gases at a flow rate of 30 000 h<sup>-1</sup>.

## DISCUSSION

The literature data [4, 25] permit one to suggest that isolated ions Cu<sup>2+</sup> in Cu-ZSM-5 catalysts are responsible for reduction of NO<sub>x</sub> with hydrocarbons. In the presence of water vapor, the zeolite is dealuminated [7, 18, 22] and the state of copper changes irreversibly [18, 26], which may result in following action of copper with Al<sub>2</sub>O<sub>3</sub> [22, 23, 27, 28] formed upon dealumination. However, XRD data of this work and ref. [22] do not show changes in the crystallinity of ZSM-5. On long storage in air [1], Cu-ZSM-5 can undergo aging resulting in formation of the clustered copper as inactive CuO.

A stabilizing effect of cerium ions on the activity of Cu-ZSM-5 in the presence of water vapor can be attributed to the suppression of both formation of CuO-like clusters and dealumination of the zeolite. After removal of water vapor from the gas phase at temperatures below 500 °C, the initial activity of the cerium modified Cu-ZSM-5 catalyst [18] partially reduces. According to ref. [19] and our data, the catalyst activity restores completely. Note that as the concentration of cerium increases, its stabilizing effect in the presence of water vapor improves [18]. Increasing the concentration of copper in Cu-ZSM-5, it is also possible to slightly increase its stability [18]. Cerium doping of Cu-ZSM-5 probably hinders migration of Cu<sup>2+</sup> to the zeolite surface and formation of CuO. A slowing down in the

formation of surface clusters CuO was confirmed by the absence of changes in the atomic ratio Cu/Si, which was observed by XPS of the modified Cu-ZSM-5 catalysts subjected to different treatments [18, 29].

On the other hand, water vapor (the reaction temperature is ~400 °C) is responsible for a decrease in the number of aluminum tetrahedrally coordinated cations at the expense of dealumination of the zeolite [3, 7, 18]. In this case, the zeolite crystal structure does not practically change. Ion Ce<sup>3+</sup> partly situated on the ion-exchange positions interacts with ion Al<sup>3+</sup> in its tetrahedral positions to hinder diffusion of aluminum from these positions into the octahedral positions as in the case of stabilization of low-temperature  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [30]. In addition, the ion-exchanged cerium may lower the zeolite dealumination, caused by hydrolysis in the presence of water vapor. Similar effect of a decrease in the dealumination degree was observed in the case Cu-ZSM-5 in the presence of 2 % H<sub>2</sub>O, compared to H-ZSM-5 [23].

Stability of the cerium modified zeolite catalyst in the presence of water vapor is apparently provided by two facts: occupation of the ion-exchange positions with cerium cations, which hinders the catalyst dealumination, and presence of the surface CeO<sub>2</sub> phase, which hinders formation of clusters CuO.

The titania modified zeolite catalysts are more resistant to sulfur poisoning [15, 31], which is probably associated with the fact that sulfation of the high disperse anatase is similar to that of copper and aluminum oxide yielding titanyl sulfate. We suggest that titanium oxide in the catalyst results in a decrease in the portion of sulfur interacting with copper cations in the zeolite. For this reason, the titanium modified zeolite catalysts are only partially stabilized in the presence of hydrogen sulfide. In contrast to TiO<sub>2</sub>, the titanium oxide modified with a sulfate ion [32] exhibits a rather high activity on the selective reduction of NO with propane especially at a temperature range of 400–600 °C. This observation was attributed a change in the oxidation ability of TiO<sub>2</sub> with respect to hydrocarbons. Thus an increase in the stability of titania modified zeolite catalysts to sulfur poisoning can be also caused by

formation of sulfated TiO<sub>2</sub> contributing to the total catalyst activity on SCR NO<sub>x</sub> with propane.

So, the composition of the modified monolith zeolite catalysts, synthesized by the ion exchange method described elsewhere [1, 2], provides their stable operation in the presence of water vapor and sulfur when the conditions of the reaction performance and catalyst treatment are properly chosen.

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