NO$_x$ Storage and Reduction over Al$_2$O$_3$ - BaO Catalyst

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Abstract

The preliminary studies of Al$_2$O$_3$ – BaO catalyst for storage and reduction of NO$_x$ in exhaust gases at rich and lean fuel mixture were performed. The conversions of nitrogen oxides as a function of fuel mixture composition were determined.

Keywords: nitrogen oxides, exhaust gases, reduction-storage catalyst

Introduction

Transportation based on the internal combustion engine has had great impact on the environment because of the 60% total emission of nitrogen oxides. EU countries constantly sharpen regulations of harmful matter emissions from exhaust gases. To fulfill new regulations, new catalytic converters based on the storage reduction mechanism are being developed [1-3].

The removal of NO$_x$ from exhaust gases of spark ignition engines have been performed by three-way catalyst. These kinds of catalyst can act close to the stochiometric air-to-fuel ratio (λ=1). For lean fuel mixtures (λ>1), three-way catalysts do not remove NO$_x$.

The advantage of a lean fuel mixture is lower fuel consumption. A lot of work has been done to find a system that can remove NO$_x$ from exhaust gases after burning a lean fuel mixture. The solution is a storage-reduction catalytic reactor working with system changing fuel mixture from lean to rich. During the lean fuel mixture period (minutes) nitrogen oxides are stored as nitrates and then reduced to nitrogen, during rich fuel mixture period (fraction of second). As a storage component of the catalyst barium compounds are used.

This mechanism may be presented as below
Each catalyst consists of:
- support for example: Al$_2$O$_3$,
- noble metals such as Pt, Pd, Rh, which during lean period oxidize NO to NO$_2$ and reduce NO$_2$ to N$_2$ during rich period [4,5,6]

- oxides of alkaline earth metals and rare earth elements, i.e. Ba, Sr, Ca, Ce, La forming with NO$_2$ nitrates acting as a trap.

Studies of different catalyst formulations based on barium and noble metals revealed that the most interesting are systems Pt/BaO/Al$_2$O$_3$ and Pd/BaO/Al$_2$O$_3$ [7]. At 300°C the first system has higher storage capacity of NO$_x$ than the second but at 400°C the relation is reversed.

Pt better than Pd catalyze oxidation of NO to NO$_2$. On the catalyst the following reactions can take place:
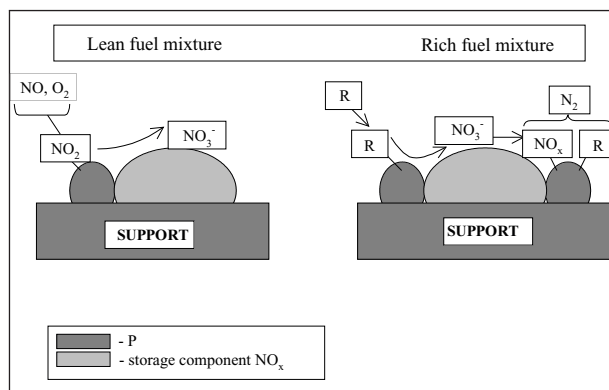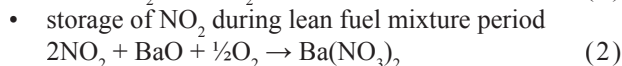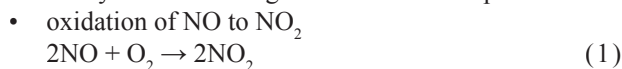- oxidation of NO to NO$_2$
$$2NO + O_2 \rightarrow 2NO_2 \tag{1}$$
- storage of NO$_2$ during lean fuel mixture period
$$2NO_2 + BaO + \tfrac{1}{2}O_2 \rightarrow Ba(NO_3)_2 \tag{2}$$

Fig.1. The mechanism of NO$_x$ storage and reduction.

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- decomposition of NO_3^- by CO (during rich fuel period)

$$Ba(NO_3)_2 + 3CO \text{ (or CO)} \rightarrow BaO+$$
$$+2NO \text{ (or } 2NO_2) + 3CO_2 \text{ (or CO}_2) \quad (3)$$

- decomposition of NO_3^- by H_2 (during rich fuel period)

$$Ba(NO_3)_2 + 3H_2(\text{or } H_2) \rightarrow BaO+$$
$$+ 2NO(\text{or } 2NO_2) + 3H_2O(\text{or } H_2O) \quad (4)$$

- reduction of NO_2 and NO (during rich fuel period)

$$NO_2 + CO \rightarrow NO + CO_2 \quad (5)$$
$$NO + CO \rightarrow \tfrac{1}{2} N_2 + CO_2 \quad (6)$$

All above reactions take place on catalyst, which contains barium compounds and noble metals. Noble metals catalyse oxidation of NO to NO_2 during lean fuel mixture and next reduces NO_2 to N_2 during rich fuel mixture. Sulphur in fuel is dangerous for catalysts because during the lean mixture phase it is oxidized and forms sulphate, which blocks nitrogen oxides traps. Barium sulphate can be reduced to barium oxide during the rich period, but generally sulphur decreases conversion of NO_x [8,9].

Alumina is used as a support of many catalysts. The thermal analysis of alumina and barium oxide mixtures revealed that above 600°C the formation of barium aluminate begins [10,11]. Barium aluminate is a better sorbent of NO_x than the barium oxide. Barium oxide forms with carbon dioxide barium carbonate, which decreases NO_x sorption. Barium aluminate does not react with carbon dioxide, which is always present in the exhaust gases. The temperature of the alumina and barium oxide mixture calcination effects composition of the product [10].

In this paper the conversion of the nitrogen oxides from spark ignition engine over BaO- Al_2O_3 catalyst was studied.

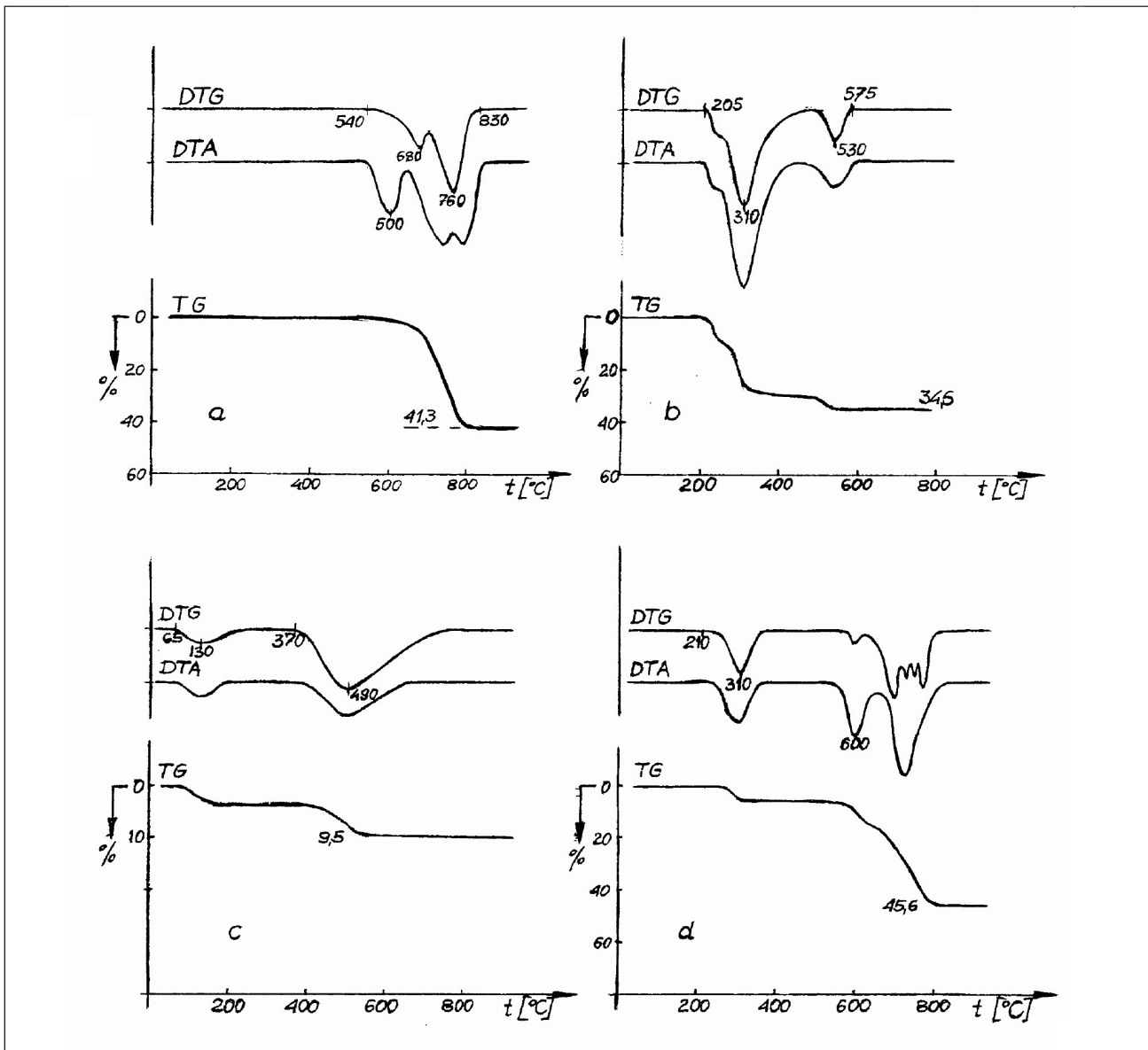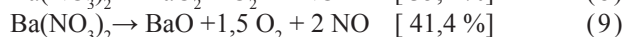Fig.2. The thermal analysis of: a)$Ba(NO_3)_2$, b) $Al(OH)_3$, c) γ Al_2O_3, d) mixture $Ba(NO_3)_2 + Al(OH)_3$ samples.

Experimental
Catalyst

The catalyst was prepared by impregnation method. γ-Al$_2$O$_3$ alumina spheres diameter 5 mm (specific surface area 250 m^2/g) delivered by Institute of Fertilisers in Puławy were immersed for 2 hours in solutions of 66 g/dm^3 Ba(NO$_3$)$_2$. After removed from the solution, spheres were dried for 24 hours at 120°C. The spheres contained 2.2% of barium. Before calcination the thermal analysis (DTA and DTG) of: a) Ba(NO$_3$)$_2$, b) Al(OH)$_3$, c) γ-Al$_2$O$_3$, d) mixture Ba(NO$_3$)$_2$ + Al(OH)$_3$ were done. Complex thermal analysis was performed with the aid a Paulik-Paulik Erdey Derivatograph produced by MOM Budapest, which enables simultaneous recording of T, TG, DTA and DTA curves. Heating rate was 9 deg/min. Results are presented in Fig.2.

Fig.2a shows that anhydrous Ba(NO$_3$)$_2$ melts at 600°C and decomposes at the temperature range 540-830°C. Decomposition is probably a multistep process going through Ba(NO$_2$)$_2$ and BaO$_2$ to BaO. The mass losses are, respectively:

$$Ba(NO_3)_2 \rightarrow Ba(NO_2)_2 + O_2 \qquad [\,12,2\,\%] \qquad (7)$$
$$Ba(NO_3)_2 \rightarrow BaO_2 + O_2 + 2NO \qquad [\,35,2\,\%] \qquad (8)$$
$$Ba(NO_3)_2 \rightarrow BaO + 1,5\ O_2 + 2\ NO \qquad [\,41,4\,\%] \qquad (9)$$

Decomposition of Al(OH)$_3$ takes place at the temperature range 205-575°C (Fig.2b). The mass loss 34.2% corresponds to total dehydration to Al$_2$O$_3$. The thermal analysis curves of γ Al$_2$O$_3$ used in experiments are presented in Fig.2c. Before the analysis γ Al$_2$O$_3$, spheres were ground. Water loss from the sample takes place from 65°C into 900°C, going through two maximums

Table 1. Phase composition and surface area of barium aluminas calcined at different temperatures [10].

T / °C	Composition of the product	S$_{BET}$ / m^2/g
800	BaAl$_2$O$_4$, Al$_2$O$_3$	161
1000	BaAl$_2$O$_4$, BaAl$_{12}$O$_{19}$ (traces), Al$_2$O$_3$	90
1200	BaAl$_{12}$O$_{19}$, BaAl$_2$O$_4$ (traces)	19

at 130°C and 490°C. The first maximum is connected to desorption of physically adsorbed water. The second, starting at 370°C, is related to desorption of chemically bonded water. Fig. 2d presents reaction of Al(OH)$_3$ and Ba(NO$_3$)$_2$ at molar ratio 1.0:1.5. Initial effects at temperature range 210-400°C with a maximum at 310°C can be attributed to dehydration of Al(OH)$_3$ further effects at 550 to 800°C to decomposition of Ba(NO$_3$)$_2$ and reaction of decomposition product with alumina leading to formation of BaAl$_2$O$_4$.

Based on these results we choose the temperature of calcination 800°C. The spheres were heated through 3 hours starting from 500°C and ending at 800°C. The reaction products were studied by X-ray phase analysis using HZG 4 apparatus, Freiberg Prezision Mechanik, Germany. XRD patterns of the samples before and after impregnation are presented in Fig.3.

XRD pattern of the sample γ-Al$_2$O$_3$ after impregnation by Ba(NO$_3$)$_2$ and calcination at 800°C is presented in Fig.4.

The XRD pattern shows only the presence of γ-Al$_2$O$_3$, but it can be result from amorphous structure [10,11] of barium aluminate.

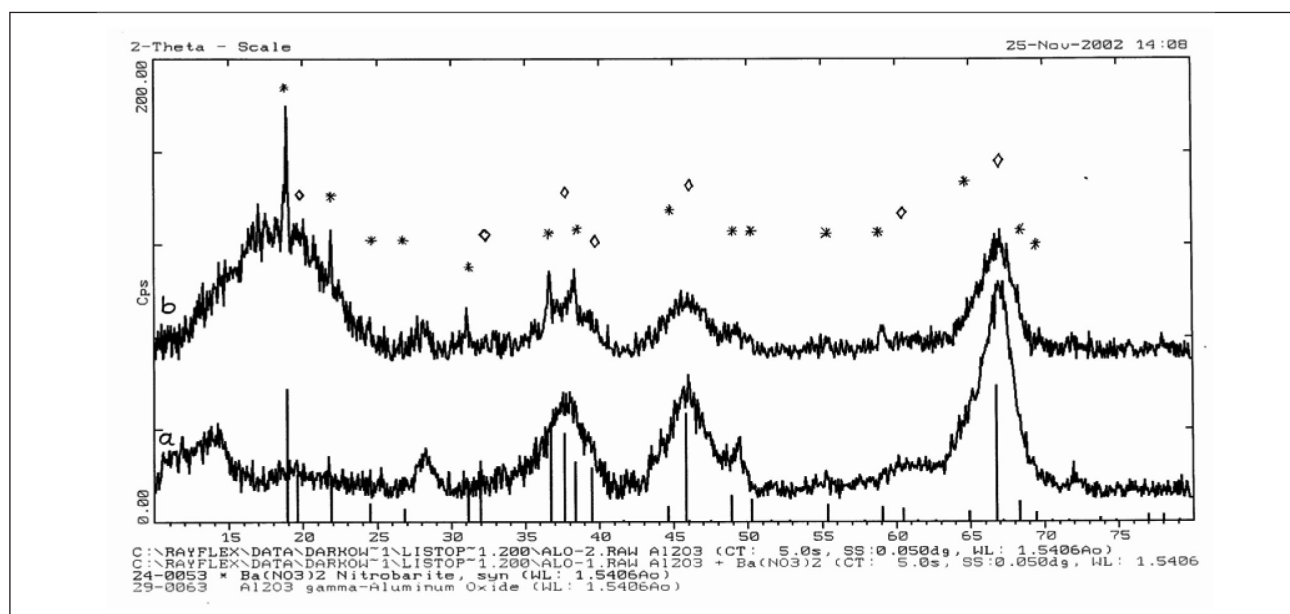Fig.3 XRD pattern of the samples γ-Al$_2$O$_3$ before (a) and after impregnation by Ba(NO$_3$)$_2$ (b); (◊ peak characteristic for γ-Al$_2$O$_3$; ∗ peak characteristic for Ba(NO$_3$)$_2$).
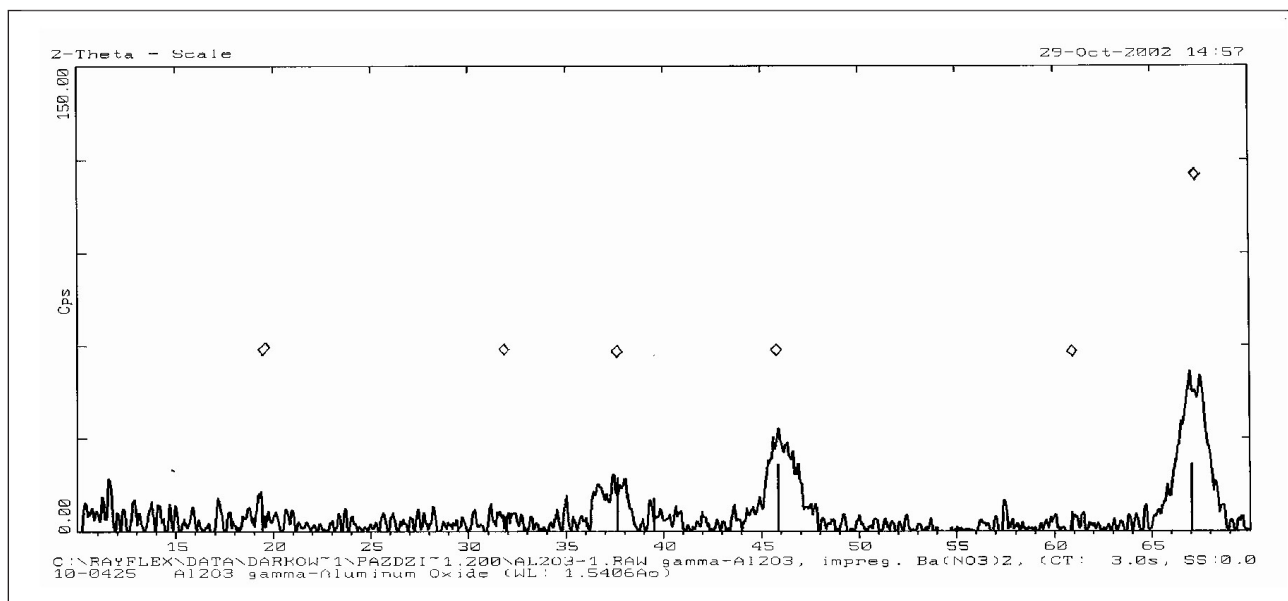
Fig.4. XRD pattern of γ-Al$_2$O$_3$ after impregnation by Ba(NO$_3$)$_2$ and calcination at 800 °C.

The spheres were inserted into the reactor diameter 35.5mm. The volume of the packing was 0.075dm^3. The spheres contained 2.17% Ba.

Studies of Storage-Catalytic Properties of Al$_2$O$_3$ – BaO System in Respect to NO$_x$

The above catalyst was tested in the system containing the following elements:
- spark ignition engine driving current generator – HONDA EM650Z
- exhaust gases analyzer – OLIVER K90
- nitrogen oxides analyzer – MADUR GA-20
- oven with temperature control panel
- quartz tube with Al$_2$O$_3$-BaO system

Studies were carried at a constant load of 100 W. The Al$_2$O$_3$ – BaO system was subjected to examination at alternating composition of the exhaust gases. It was achieved by closing and opening valve, allowing extra air to get to the space between carburettor and engine. Studies were done in repeating periods :
- 60s of rich fuel mixture (λ=0.92) average composition NO=111 ppm; HC=231 ppm; CO=3.38%; CO$_2$=12.6%; O$_2$=0.77%
- 120s of lean fuel mixture (λ=1.14) average composition NO=86 ppm; NO$_2$=2 ppm; HC=262 ppm; CO=0.43%; CO$_2$=12.5%; O$_2$=3.28%.

Results

The dependence of NO$_x$ concentration on the exhaust gases composition and time at 300°C is shown in Fig.6.

From data in Fig.6 the degree of NOx removal were calculated and they are presented in Fig.7.

The degree of NO$_x$ removal is calculated using the following equation:

$$K_{(NO)} = [C_{(NO)i} – C_{(NO)f}]/C_{(NO)f}$$

Where C$_i$ is the initial (at he reactor inlet) and C$_f$ the final (at the reactor outlet) concentration. The term "degree of NO$_x$ removal" is understood here as the effect of storage process and reduction process. During the change from lean to rich fuel mixture there is a rapid increase of NO concentration (Fig.6). This can be caused by first step of reduction of nitrates to NO (eqs. 3-4). The results
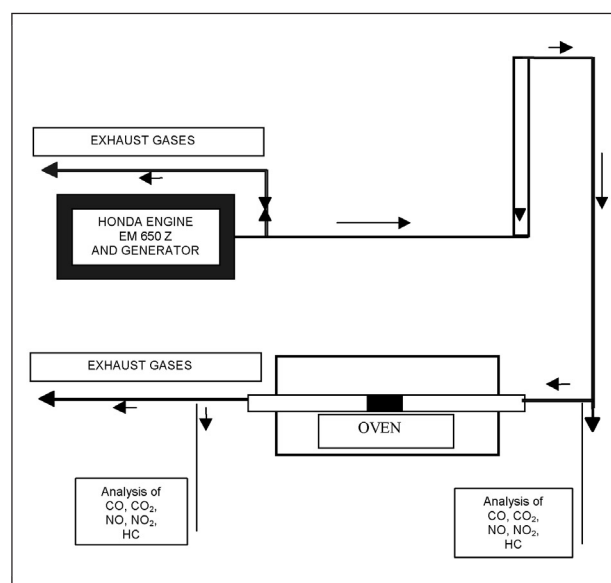

Fig.5. Stand for the storage-reduction activity measurement of the catalyst.
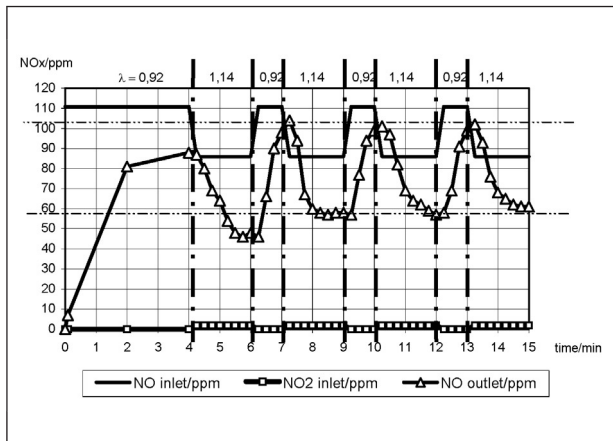
Fig.6. The dependence of NO_x concentration before and after the catalyst for the lean and rich fuel mixture. Catalyst temperature is 300°C.
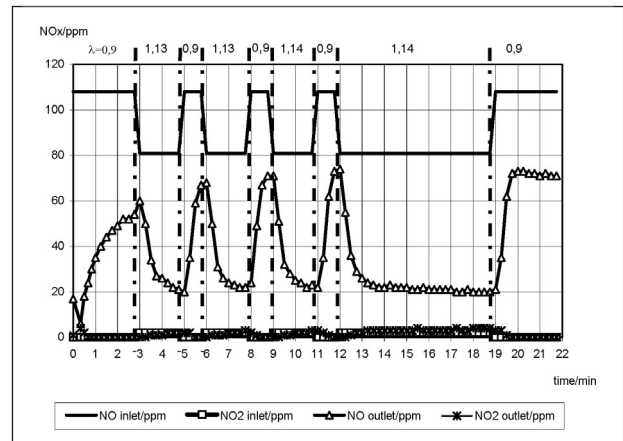

Fig. 8. The dependence of nitrogen oxides concentration on the fuel mixture composition at 400 °C.
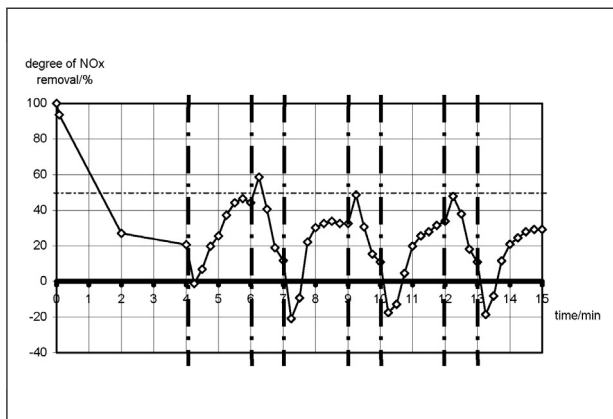

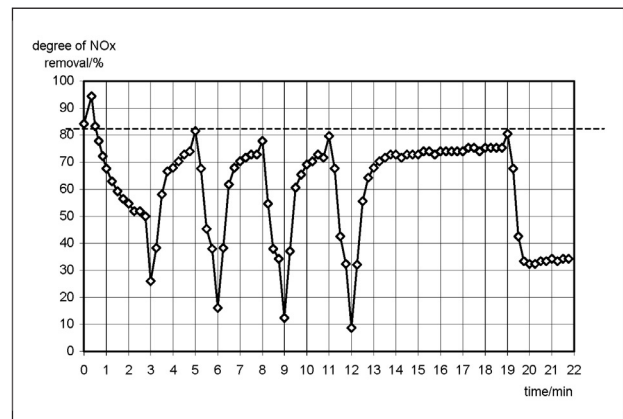Fig.7. The degree of NO_x removal calculated from Fig.6. data.

Fig.9. The degree of nitrogen oxides removal as the function of fuel mixture composition at 400 °C.

obtained at 300 °C show a low degree of NO_x removal not exceeding 50%. There is no NO_2 in the exhaust gases.

Similar studies were carried out at 400°C. The dependence of nitrogen oxides concentration on changes of fuel mixture composition is shown in Fig.8.

From data in Fig.8 the degree of NO_x removal were calculated. They are presented in Fig. 9.

At 400 °C the NO_x concentration during lean mixture period falls to 21 ppm from 80 ppm. The maximum degree of NO_x removal is higher (70%) than at 300 °C.

The maximum storage capacity of the system was evaluated in the following experiment: exhaust gases from lean fuel mixture were flowing over catalyst until an increase of nitrogen oxide was detected. The load of the generator was 300 W, so nitrogen oxide concentration was 198 ppm. After 37 minutes an increase of NO concentration was detected. It allowed to calculate the total amount of reduced and stored nitrogen oxide. It is 0,581 mmol NO or 0,0103 mmol per gram of the catalyst. It is 1/3 of the value presented in [3] but it can be

caused by smaller barium concentrations and the use of real exhaust gases.

Conclusion

- Al_2O_3 – BaO system is able to store and reduce NO from real exhaust gases (from spark ignition engine).
- The degree of NO_x removal was determined. NO_x removal is understood as a result of storage of NO_x as nitrate and reduction of NO_x to nitrogen.
- Activity of the catalyst should be improved by adding components that can catalyse oxidation of NO to NO_2. Noble metals can be used as such components.

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