REMOVAL OF NITROGEN OXIDES OVER CATALYST BY CHANGING EXHAUST GASES COMPOSITION

Małgorzata Księżopolska, Andrzej Darkowski
Wioletta Raróg-Pilecka, Dominika Dłuha

Faculty of Chemistry, Warsaw University of Technology
Noakowskiego 3, 00-664 Warsaw, Poland, tel.:48 22 660-79-73
e-mail: malgorzata.ksiezopolska@ch.pw.edu.pl, dark@ch.pw.edu.pl

Abstract

The influence of addition of potassium or barium to Pd/Al_2O_3 catalyst on the catalytic performance of nitrogen oxides storage-reduction catalyst was studied. The catalysts: $Pd-K-Al_2O_3$, $Pd-Ba-Al_2O_3$ and $Pd-K/Ba-Al_2O_3$ were prepared by impregnation method. Alumina spheres contained Pd=1 and 4 %, K=10%, and/or Ba=10%. The conversions of nitrogen oxides as function of fuel mixture composition were determined. Studies were carried at the temperature range 200-500ºC. The influence of addition of potassium and barium to catalyst on its storage-reduction nitrogen oxide activity was considered. The highest conversion of NO_x was obtained for $Pd(4\%)-K-Al_2O_3$ catalyst. Results show that the highest conversion of NO_x was obtained for $Pd^{(4\%)}-K-Al_2O_3$ catalyst it could be caused with different structure of catalyst surface. For all catalysts, during periodic changes of lean to rich mixture, NO_x conversion is high during lean condition and is falling during rich condition and is later increasing repeatedly. catalysts composition influences the temperature range in which its activity is the highest. On the base of studied data conversion of NO_x there was observde that catalysts composition influences the temperature range in which its activity is the highest. Although dispersion of palladium decreases when its concentration increases, a fall of nitrogen oxide conversion for catalysts containing higher concentration of palladium does not occur.

Keywords: barium; potassium; NO_x; Pd; NO_x storage-reduction; catalytic reactor

1. Introduction

Emission limits and fuel saving trends caused development of engines which can burn lean fuel mixtures (air/fuel > 20.0) e.g. diesel engines and lean-burn spark ignition engines. It can reduce the fuel consumption and provide more efficient combustion in comparison with a stoichiometric operating engine system but decreases efficiency of NO_x removing. Removing of NO from exhaust gases at oxygen presence can be done by selective catalytic reduction of NO_x by hydrocarbons [1]. Unfortunately there is no catalyst able to work efficiently at wide range of temperature. The problem can be solved by nitrogen oxides storage-reduction system (NSR) [2-4]. There is a sorption of NO_x during lean condition and desorption and reduction during rich condition [5-6]. The mechanism of NO_x storage may look as presented on Fig. 1 [7].

Noble metals during lean period oxidize NO to NO_2 and reduce NO_2 to N_2 during rich period. Compounds of alkali metals and alkaline earth group metals are used as a storage component of the catalyst. Compounds of these elements have been proven effective in forming nitrates with NO_2 that are released and reduced during rich period.

There are many parameters affecting the catalytic activities of NO_x storage and reduction catalysts; for example: reaction temperature, times of storage and reduction, exhaust gases composition and catalytic composition, dispersion of noble metals or surface area. This paper examines the influence of storage components and concentration of noble metals on storage and reduction properties of NO_x present in real exhaust gases. Catalytic NO_x storage and reduction activities of $Pd-K-Al_2O_3$, $Pd-Ba-Al_2O_3$ and $Pd-K/Ba-Al_2O_3$ were measured.

M   Pt Rh Pd

storage component (component of alkali metal and alkaline earth group metals)

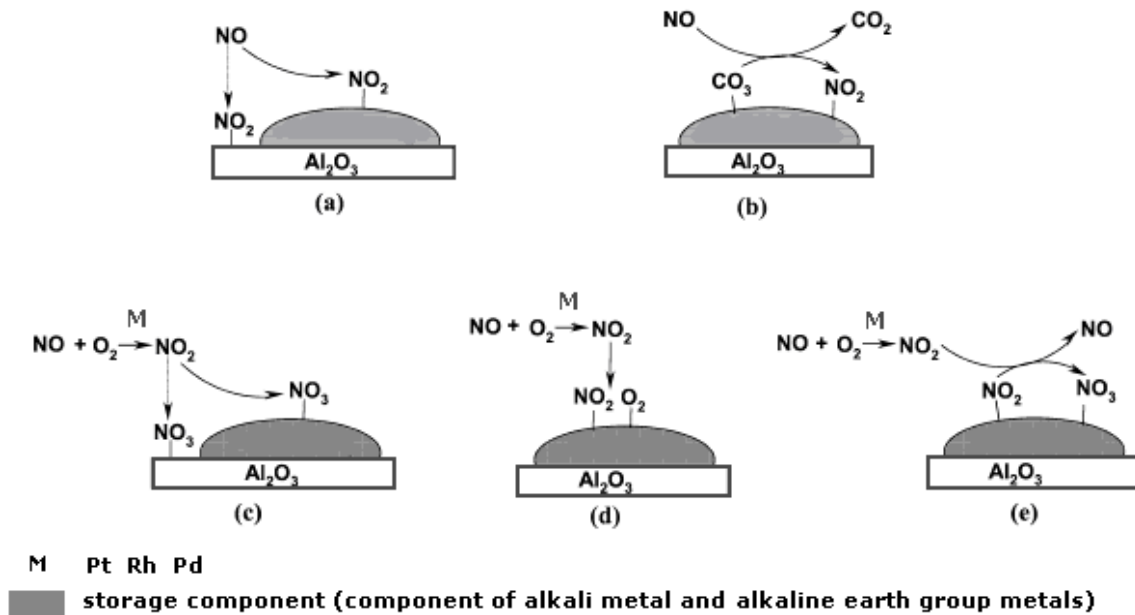*Fig.1. Scheme of the main elementary steps for NO_x storage. (a) formation of nitrites by molecular adsorption of NO; (b) replacement of Ba carbonates with Ba nitrites formed by NO; (c) formation of nitrates by molecular adsorption of NO_2; (d) formation of Ba nitrites and Ba peroxides by dissociative adsorption of NO_2; (e) transformation of surface nitrites to surface nitrates with NO_2 as oxidizing agent [7]*

2. Experimental

2.1. Catalysts preparation and activity study

Alumina spheres ø 2-5 mm (specific surface area 350 m^2/g) delivered by Merck were immersed for 0,5 hours in solution of H_2PdCl_4. After removing from the solution spheres were dried for 24 hours at 120^oC and reduced in H_2 stream at 500^oC. Potassium and barium was introduced by impregnation Pd/Al_2O_3 spheres in KOH and/or $Ba(NO_2)_2$ solution. Impregnation by different barium salt - $Ba(NO_3)_2$ also was studied [8]. Concentration of Ba in that catalyst was low (~3 %) and didn't obtain agreeable results of NO_x conversion in lean condition.

The composition of the catalysts was as following Pd=1 and 4 %, K=10%, Ba=10%. The above catalysts were tested in the atmosphere of real exhaust gases from spark ignition engine in the system containing the following elements:
- spark ignition engine driving current generator
- exhaust gases analyser – CO, CO_2, hydrocarbon were determined by non dispersive IR analysis, O_2 by electrochemical sensor,
- nitrogen oxides analyser – NO and NO_2 by electrochemical sensors,
- oven with the temperature control panel
- quartz tube with inner diameter 40 mm with the catalysts

Catalysts were examined with an oscillation between the rich and lean conditions with rich/lean time 1/3 minutes. The switch between rich (λ=0.9; HC=415 ppm; CO=3.9 %; CO_2=12.5 %; NO_x=95 ppm; O_2=0.7 %) and lean (λ=1.5; HC=570 ppm; CO=0.55 %; CO_2=10.8 %; NO_x=75 ppm; O_2=5.2 %) fuel mixture was realized by opening and closing a valve and allowing extra air to get to the space between carburetor and the engine. All experiments were carried out with a total flow rate through the reactor of ~5 dm^3/min (SV=7000 h^{-1}). Palladium dispersion was measured for different catalyst composition and palladium concentration.

2.2. SEM analysis and palladium dispersion

The structure of the catalytic layer was studied by SEM. The microstructure $Pd^{(4\%)}$-$Ba^{(10\%)}$-Al_2O_3, $Pd^{(4\%)}$-$K^{(10\%)}$-Al_2O_3 and $Pd^{(4\%)}$-$K^{(10\%)}$/$Ba^{(10\%)}$-Al_2O_3 was investigated using MM-40 Nikon scanning electron microscope.

The examinations were carried out in a conventional, fully automated temperature-programmed set-up (manufactured by Technical University of Łódź), equipped with a U-tube reactor and a TCD cell [9]. Prior to measurements, the samples were reduced in a H_2 : $Ar = 80 : 20$ mixture (40 ml/min) at 500^oC for 16 h and, after flushing with argon at 500^oC (40 ml/min, 30 min), were cooled in a Ar stream. Then, the hydrogen uptake was measured at 70^oC by adding H_2 pulses (2.28 μmol) to flowing argon [10]. The uptakes of an adsorbate was used for determining the dispersion of palladium (FE – fraction exposed) and size of the metal particles (d). The latter parameter was calculated from the generalized formula proposed by Borodzinski and Bonarowska [11]. The H : Pds = 1 :1 stoichiometry of adsorption was assumed to recalculate the adsorbate uptake into the FE value.

3. Results

3.1. Characterisation study resultes

The SEM photomicrographs are shown in Fig. 2. whereas the quantitative microanalysis data for $Pd^{(4\%)}$-$Ba^{(10\%)}$-Al_2O_3 and $Pd^{(4\%)}$-$K^{(10\%)}$-Al_2O_3 catalysts are summarised in Tab. 1.
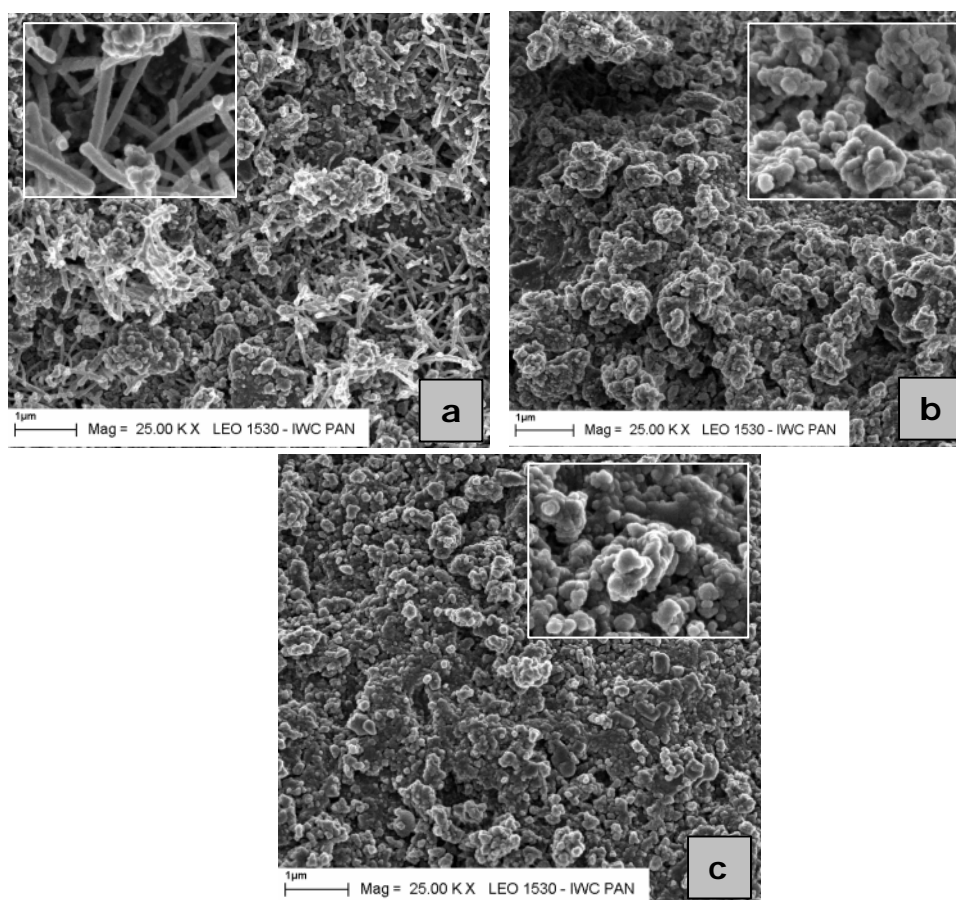
Fig. 2. SEM photomicrographs of a) Pd-K-Al₂O₃, b) Pd-Ba-Al₂O₃ and c) Pd-K/Ba-Al₂O₃

The Pd-Ba-Al$_2$O$_3$ and Pd-K/Ba-Al$_2$O$_3$ surfaces are similar (Fig. 2b and 2c) nevertheless for the Pd-K-Al$_2$O$_3$ catalyst it can be observed significant differences (Fig.2a).

On the basis of microanalysis that was repeated for each sample in three different points (Tab. 1), we can observe concentrations of different elements on the catalysts surface. The Pd-Ba-Al$_2$O$_3$ catalyst surface contained less than 10% of storage component (7.8-9.2 %) but concentration of palladium was about 4%. Different situation was observed for the Pd-K-Al$_2$O$_3$ catalyst where the concentration of palladium was lower than on the Pd-Ba-Al$_2$O$_3$ catalyst (2.5-3.0 %) but the storage component concentration was very similar for each three points (~ 10 %).

Tab. 1. Point microanalysis of Pd-Ba-Al$_2$O$_3$ and Pd-K-Al$_2$O$_3$

element	Pd-Ba-Al$_2$O$_3$			Pd-K-Al$_2$O$_3$		
Wt / %	point 1	point 2	point 3	point 1	point 2	point 3
C	7.4	10.3	11.5	13.2	13.8	13.2
O	41.9	40.2	40.2	43.4	42,8	41.9
Na	3.4	4.1	3.2	0.21	0.2	0.3
Al	30.2	28.9	28.4	30.3	30.1	30.5
Cl	3.5	4.1	3.2	0.2	0.1	0.2
Pd	4.2	4.1	3.2	2.5	2.8	3.0
Ba	9.2	7.8	8.6	--	--	--
K	--	--	--	10.0	10.0	10.8

Table 2 summarizes the H$_2$ chemisorption results, expressed via both, the fraction exposed (FE) and metal particle size (d). As expected, the Pd-Al$_2$O$_3$ catalyst of high Pd loading (4 %) has a lower dispersion (FE = 0.22) than the system of low metal loading (FE = 0.28 for 1 % Pd). The effect of an additive is dependent on its kind. Whereas barium seems not to change the Pd dispersion (see Table 2), potassium reduces the FE value by about 30 %, compared to the additive-free material. It is a rather open question, whether the potassium presence leads to sintering the Pd crystallites or site blocking, thus making some of the surface Pd atoms to be inaccessible for hydrogen.

Tab.2 Dispersion of palladium (FE) and metal particle size (d) in the alumina supported catalysts

CATALYST	FE	d /nm
Pd$^{(1\%)}$-Al$_2$O$_3$	0.28	4.4
Pd$^{(4\%)}$-Al$_2$O$_3$	0.22	5.8
Ba-Pd$^{(1\%)}$-Al$_2$O$_3$	0.26	4.8
K-Pd$^{(1\%)}$-Al$_2$O$_3$	0.20	6.5

3.2. Activity of the catalysts

More information about the storage of NO$_x$ on these catalysts was obtained by repeating the lean/rich cycles using real exhaust gases. Repeating these lean/rich cycles took place at a different temperature level (for catalysts with barium at the temperature range 200-400°C; with potassium at 300-500°C and with barium and potassium at 200-500°C).

Pd-Ba-Al$_2$O$_3$

Figure 3 shows the NO$_x$ conversion over Pd-Ba-Al$_2$O$_3$ catalysts (Fig.3a Pd(1%)-Ba-Al$_2$O$_3$ and Fig.3b Pd(4%)-Ba-Al$_2$O$_3$ catalyst). The highest storage-reduction NO$_x$ activity was observed for

Pd(4%)-Ba-Al$_2$O$_3$ catalyst at 300°C. For both catalysts the NO$_x$ conversion was high up to 1.5-2 minutes when fuel mixture was changed from rich to lean, but fell during next two minutes. After switching to rich condition the NO$_x$ conversion was continually decreasing and after several seconds NO$_x$ conversion increased again. Explanation of this fact may be as follows: after switching to rich condition the nitrate, which was formed during lean condition, was reduced to nitric oxide and therefore a sudden increase of nitric oxide at gas phase appeared. Next, the nitric oxide was reduced in non-selective reduction.

The lowest NO$_x$ conversion for this catalyst was observed at 400°C. In that temperature the degree of NO$_x$ conversion was lower after every cycle. It can be explained by high temperature storage capacity of Pd-Ba-Al$_2$O$_3$ catalyst and it's capability to reduced nitrogen oxide adsorbed during lean condition decreased. The catalyst with 4 % concentration of palladium (Fig.3b) showed higher NO$_x$ conversion at the whole temperature range.
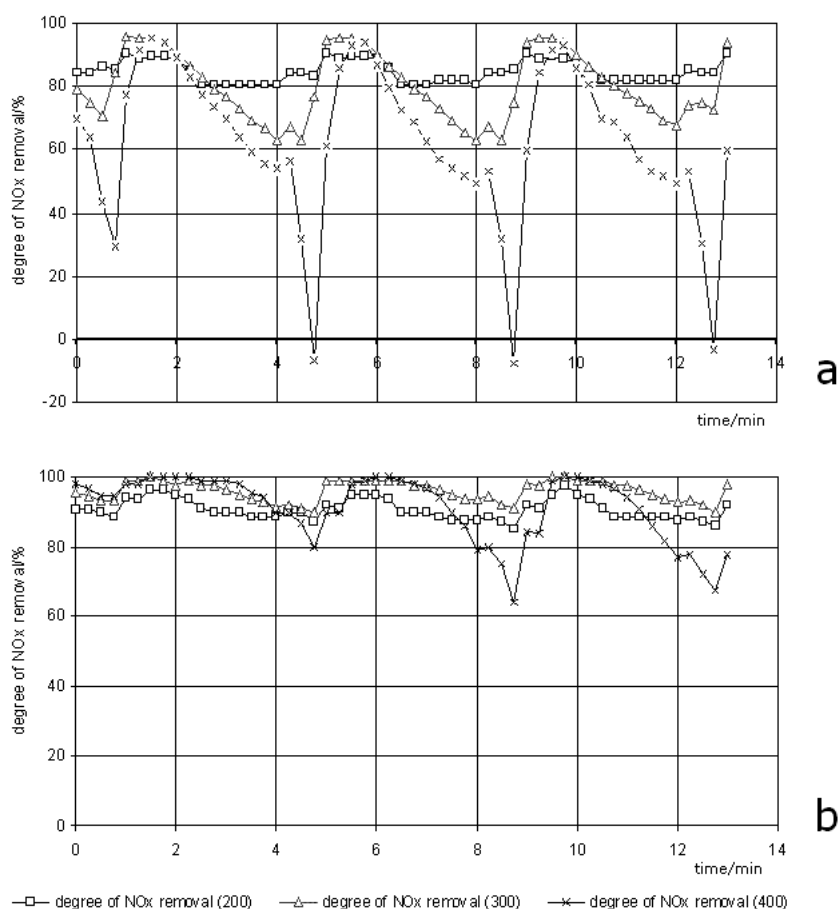

Fig. 3 The degree of nitrogen oxides removal as a function of fuel mixture composition at 200, 300 and 400°C; a- Pd$^{(1\%)}$-Ba-Al$_2$O$_3$; b- Pd$^{(4\%)}$-Ba-Al$_2$O$_3$

Pd-K-Al$_2$O$_3$

Pd-K-Al$_2$O$_3$ catalysts show the highest NO$_x$ conversion at higher temperatures in comparison to barium catalysts as in Fig. 4. The catalytic activities of Pd-K-Al$_2$O$_3$ catalysts were measured in the same lean/rich cycles at temperature range of 300-500°C. It is interesting to notice that during the whole test of these catalysts the NO$_x$ conversion did not decrease below 80% for Pd$^{(1\%)}$-K-Al$_2$O$_3$ (Fig 4a) and 90% for Pd$^{(4\%)}$-K-Al$_2$O$_3$ catalyst (Fig. 4b). The decrease of NO$_x$ storage reduction activity was not observed for each of the next lean/rich cycles. Thanks to the fact

that Pd-K-Al$_2$O$_3$ catalyst show higher capability to reduced nitrogen oxides the NO$_x$ conversion did not decrease after switching to rich fuel mixture.

The highest NO$_x$ conversion was obtained at 500°C (95-100%). Higher concentration of palladium increased catalytic activity at the temperature of 300°C; for rich and lean fuel mixture the degree of NO$_x$ conversion increased on average to 5%. Therefore the examined catalyst has a higher capability of NO$_x$ storage and NO$_x$ selective catalytic reduction (SCR-NO$_x$).
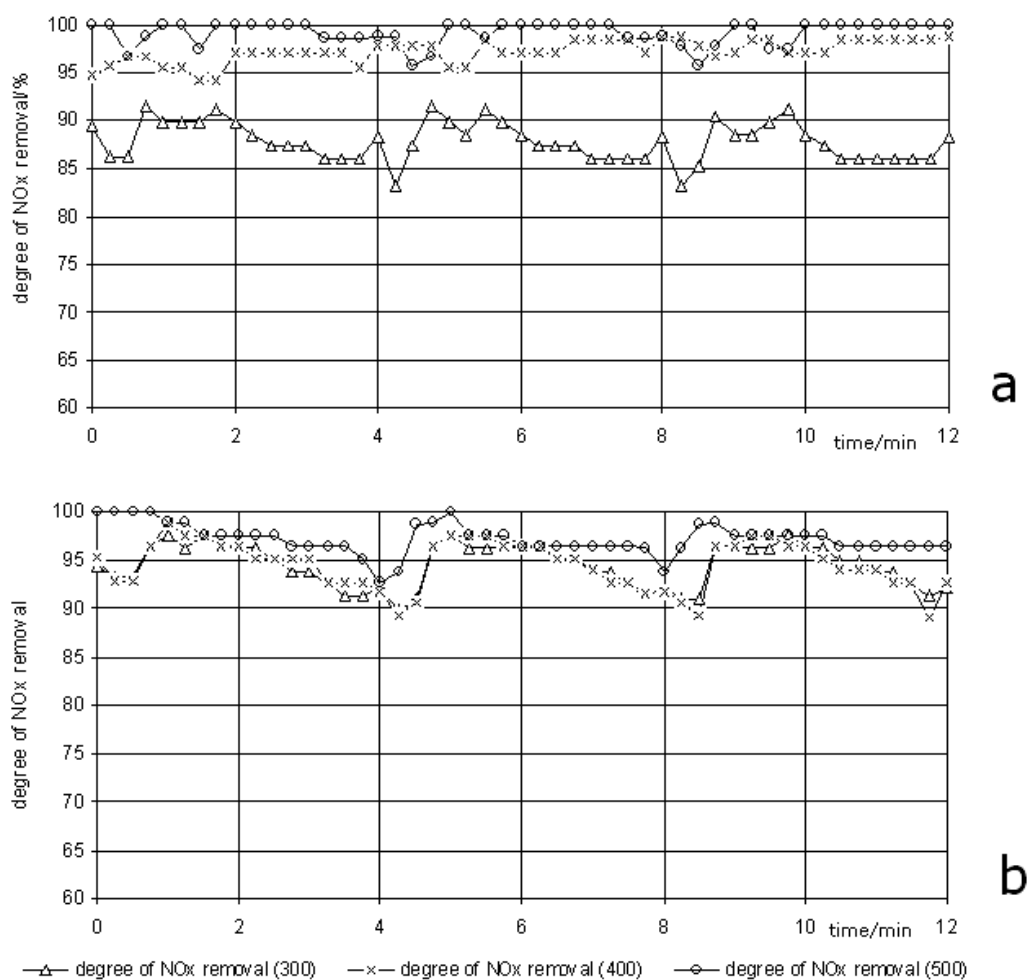

Fig. 4 The degree of nitrogen oxides removal as a function of fuel mixture composition at 300, 400 and 500°C; a- Pd$^{(1\%)}$-K-Al$_2$O$_3$; b- Pd$^{(4\%)}$-K-Al$_2$O$_3$

Pd-Ba/K-Al$_2$O$_3$

For the final set of study Pd$^{(4\%)}$-Ba/K-Al$_2$O$_3$ catalysts was examined. Figure 5 shows NO$_x$ conversion as a function of time. The study was conducted in conditions of periodic changes of lean to rich mixture. The catalytic activities of this catalyst were measured at the temperature range of 200-500°C. Addition of potassium to Pd-Ba-Al$_2$O$_3$ catalyst increased NO$_x$ conversion in comparison to Pd-Ba-Al$_2$O$_3$ catalysts. It shows that sorption capacity of NO$_x$ has increased significantly. NO$_x$ conversion increased together with the rise of the temperature. The catalyst showed low stability in lean/rich mixture cycles in comparison to Pd-K-Al$_2$O$_3$ but the decrease of NO$_x$ conversion after the release of nitrogen oxides is lower than the one observed in case of Pd-Ba-Al$_2$O$_3$ catalysts. It means that Pd-K/Ba-Al$_2$O$_3$ catalyst is able to reduce more NO$_x$ then was formed during lean conditions.
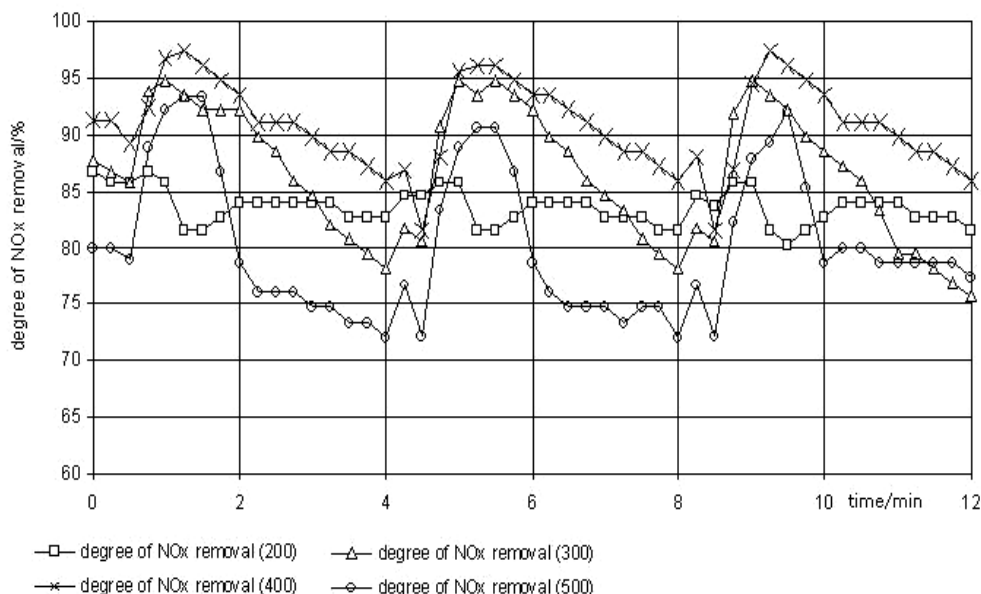
Fig. 5 The degree of nitrogen oxides removal as a function of fuel mixture composition at 200, 300, 400 and 500°C for Pd$^{(4\%)}$-Ba/K-Al$_2$O$_3$ catalyst

4. Conclusions

- Five catalysts: Pd$^{(1\%)}$-K-Al$_2$O$_3$, Pd$^{(4\%)}$-K-Al$_2$O$_3$, Pd$^{(1\%)}$-Ba-Al$_2$O$_3$, Pd$^{(4\%)}$-Ba-Al$_2$O$_3$ and Pd-$^{(4\%)}$K/Ba-Al$_2$O$_3$ were prepared.
- The influence of addition of potassium and barium into catalyst on its storage-reduction nitrogen oxide activity was studied.
- The structure of the catalytic layer was studied by SEM.
- NO$_x$ conversion was used for comparison of catalytic and sorption activity.
- The highest conversion of NO$_x$ was obtained for Pd$^{(4\%)}$-K-Al$_2$O$_3$ catalyst it could be caused with different structure of catalyst surface.
- For all catalysts, during periodic changes of lean to rich mixture, NO$_x$ conversion is high during lean condition and is falling during rich condition and later is increasing repeatedly. This can be explained by nitrate's reduction to nitric oxide so that there is a rapid increase of nitric oxide in gas phase.
- On the base of studied data conversion of NO$_x$ we can observe that catalysts composition influences the temperature range in which its activity is the highest.
- In spite the fact that dispersion of palladium decreases when it's concentration increases we do not note a fall of nitrogen oxide conversion for catalysts containing higher concentration of palladium.

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