

STUDY OF NO_x STORAGE OVER THE Pt/Rh-MgO/(CeO₂)/Al₂O₃ CATALYST

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Abstract

Preliminary studies of Pt/Rh-MgO/Al₂O₃ and Pt/Rh-MgO/CeO₂/Al₂O₃ catalysts for storage and reduction of NO_x in exhaust gases at rich and lean fuel mixture were performed. NO_x conversion and time of reaching steady state for lean mixture was used for comparison of catalytic and sorption activity. Catalysts were prepared: first on the alumina pellets by impregnation process and second on steel honeycomb monolith with washcoat layer. The conversion of nitrogen oxides as a function of temperature and different time of lean period to rich was determined. Thanks to the results of these studies both catalysts were compared.

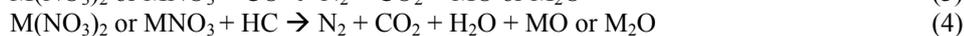
The prepared bed reactor containing magnesia as NO_x trap oxidizes CO and HC and reduces NO_x during cyclic changes of air to fuel mixtures. Oxidation and reduction properties of the reactor are strongly dependent on the cycle of mixture changes and temperature. Generally there is an average NO_x conversion ratio decrease with the increase of lean period time. For monolith type of reactor Pt/Rh-MgO/CeO₂-Al₂O₃ conversion didn't obtain acceptable results above 200°C for both SV values. The relation of the surface area to the volume of the reactor was higher for the monolith reactor than for the bed type.

Keywords: NO_x storage reduction catalyst; lean burn engines, conversion, lean mixture, rich mixture

1. Introduction

Removals 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 stoichiometric air to fuel ratio ($\lambda=1$). For lean fuel mixture ($\lambda>1$) three way catalyst do not remove NO_x. Lower fuel consumption is an advantage of lean fuel mixture. A new type of reactor, which can eliminate NO_x at oxygen presence, was developed [1]. A lot of work was done to find a system which can remove NO_x from exhaust gases after burning lean mixture. Until now no practical means of reducing NO_x by hydrocarbons at presence of oxygen was done. Reduction of NO_x at presence of oxygen is called selective catalytic reduction (SCR) and until now works for ammonia as a reductant. The use of hydrocarbons as a reductant with noble metal catalysts is effective for temperatures below 300°C [2]. Above this temperature a side reaction of oxidation of reductant by molecular oxygen takes place so that conversion ratio of NO_x decreases.

New approach to the problem was done by Toyota [3]. They proposed a storage-reduction catalytic reactor working with system changing fuel mixture from lean to rich. During lean fuel mixture period (minutes) nitrogen oxides are stored as nitrates and next they are reduced to nitrogen during rich air to fuel mixture period (fraction of second). As a storage component of the catalyst alkali metal compounds and rare earth group metals are used [4-10]. Reactions on the catalyst surface with these group metal during storage reduction cycles schematic are described as follows (1-5) [11]:





This paper presents studies on storage and reduction properties of NO_x present in real exhaust gases for catalysts containing platinum, rhodium and magnesium compounds.

Nowadays the monolithic reactors are commonly employed in car exhaust systems. The main reasons for this situation is lower gas pressure drop and mechanical hardness of the surface of the monolith. That is way two types of reactors were prepared for study and comparison of their catalytic activities in real conditions; first Pt/Rh-MgO/Al₂O₃ bed reactor and second Pt/Rh-MgO/CeO₂/Al₂O₃ monolith reactor. The bed reactor was prepared on pellets support, thanks to this comparison of hydrodynamic conditions and activities Pt/Rh-MgO/Al₂O₃ catalyst with monolithic Pt/Rh-MgO/CeO₂/Al₂O₃ is possible.

2. Experimental

2.1. Catalysts preparation

Bed reactor

The Pt/Rh-MgO/Al₂O₃ catalyst was prepared on alumina spheres \varnothing 2-5 mm (specific surface area 350 m²/g) delivered by Merck. Spheres were immersed for 0.5 hours in solution of Mg(NO₃)₂*6H₂O and next dried and calcinated in 500°C, after the calcination they were impregnated by H₂PtCl₆ and RhCl₃ solutions and reduced in H₂ stream at 500°C. After the calcinations, the specific surface area was decreased by 30% but still remained on high level – 240 m²/g. Ratio of the surface area to the volume of the reactor was calculated at 1.8 m²/dm³. The composition of the catalysts were as follows: Pt 0.27 %, Rh 0.13 %, MgO 10 %. Concentration of noble metals is low in comparison to whole mass of pellets, however, it should be noted that the active layer is only a surface coating. It is clearly shown in figure 1. Average thickness of this layer was calculated on the representative group of pellets at 0.4 mm. The volume of active layer constitutes around 47 % of the whole sphere. The concentration of noble metals per 1 dm³ of the active layer amounts to 5.8 g/dm³ of platinum and 2.9 g/dm³ of rhodium.

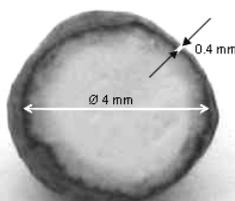


Fig.1. The cross-section of pellet of bed reactor Pt/Rh-MgO/Al₂O₃.

Monolith reactor

Catalytic reactor Pt/Rh-MgO/CeO₂/Al₂O₃ was prepared from a steel monolith. The monolith had 64 channels/cm² that were covered by a catalyst carrier (130 g/dm³) consisting of 30 % MgO, 10 % CeO₂ and 60 % Al₂O₃. The specific surface area of the dry ceramic layer amounts to 20.8 m²/g; it is around 10 times lower then the level for the bed reactor. Relation of the surface

area to the volume of the reactor was calculated at $2.1 \text{ m}^2/\text{dm}^3$, so it is higher than for the Pt/Rh-MgO/Al₂O₃ catalyst.

The carrier was impregnated by H₂PtCl₄ and RhCl₃ in the same amount as Pt/Rh-MgO/Al₂O₃ catalyst. The concentration of noble metals after reduction was Pt- $2.8 \text{ g}/\text{dm}^3$ and Rh – $1.1 \text{ g}/\text{dm}^3$ respectively. The catalytic reactor had tubular shape ϕ 28 mm and 70 mm long. The structure of the catalytic layer was studied by SEM. Fig. 2 shows SEM image of the catalyst surface.

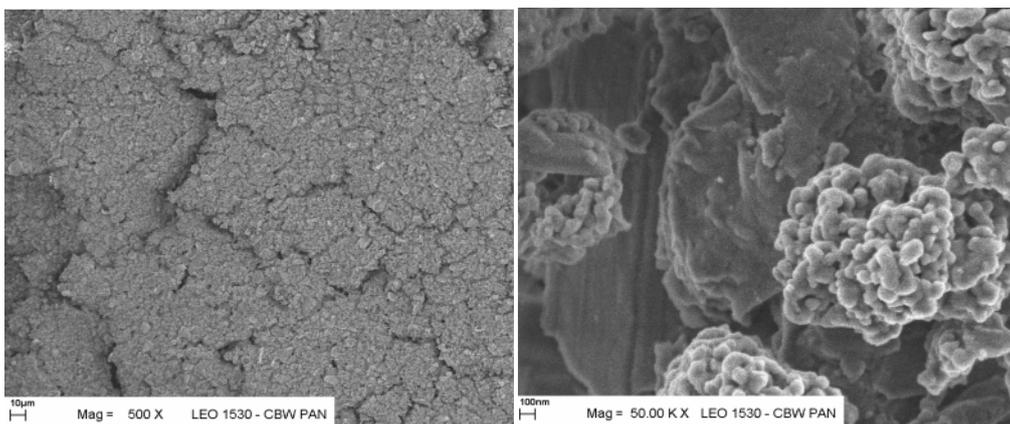


Fig.2. SEM photographs of Pt/Rh-MgO/CeO₂/Al₂O₃ catalyst surface.

2.2. Methods and the activity testing stand

The above catalysts were tested in the atmosphere of real exhaust gases from spark ignition engine in the system containing the following elements:

- the spark ignition engine driving current generator,
- the exhaust gases analyser – CO, CO₂, hydrocarbon were determined by non dispersive IR analysis, O₂ by electrochemical sensor,
- the nitrogen oxides analyser – NO and NO₂ by electrochemical sensors,
- the oven with the temperature control panel,
- quartz tube with the catalysts.

The switch between rich and lean air to fuel mixture was realized by opening and closing a valve and allowing extra air to get to the space between the carburettor and the engine. In consequence of application of real exhaust gases for studies the composition of these gases was inconstant. The average composition of exhaust gases before the catalysts for lean and rich fuel mixture was presented in table 1.

Tab. 1. The average concentration of HC, CO, CO₂, and O₂ in real exhaust gases for rich and lean mixture.

| Exhaust composition | HC /ppm | CO /% | CO ₂ /% | O ₂ /% |
|---------------------|---------|-------|--------------------|-------------------|
| lean $\lambda=1.19$ | 1000 | 0.90 | 10.00 | 4.00 |
| rich $\lambda=0.95$ | 400 | 2.30 | 13.00 | 0.80 |

The following studies were carried out:

For bed reactor:

- current HC and CO conversion in temperature range of 200-500°C,

- conversion of NO_x during simulation test of real engine working condition when gas flow was 2 (SV=3000 h⁻¹) or 5 dm³/min (SV=7000 h⁻¹) in the same range of temperature,
- current NO_x conversion and time of reaching steady state for lean mixture when gas flow was 2 or 5 dm³/min in temperature range 200-500°C.

For monolith reactor

- conversion of NO_x during simulation test of real engine working condition when gas flow was 2 (SV=3500 h⁻¹) or 5 dm³/min (SV=9000 h⁻¹) in temperature range 200-300°C.

Cycles (time of reduction + time of storage) were as following:

- cycle - 30 s (λ=0.95) + 30 s (λ=1.19),
- cycle - 30 s (λ=0.95) + 60 s (λ=1.19),
- cycle - 30 s (λ=0.95) + 90 s (λ=1.19).

3. Results

3.1. Activity of the bed reactor

Conversion of HC and CO for lean and rich mixture on Pt/Rh-MgO-Al₂O₃ catalysts, in temperature range of 200-500°C, was measured. The results are presented in table 2. Conversion of hydrocarbons increased with temperature growth equally for lean and rich mixture. Different situation was observed for carbon oxide, the highest conversion was noted in temperature range of 200-300°C, later the conversion decreased. The fall of the CO conversion at the temperature 500°C to 13.3% could have been caused by reaction of hydrocarbons with water (6) [12].



Tab. 2. The average carbon monoxide and hydrocarbons conversion ratio for different exhaust composition.

| T/°C | X _{HC} rich condition /% | X _{CO} rich condition /% |
|------|--------------------------------------|--------------------------------------|
| 200 | 3.2 | 58.8 |
| 300 | 43.7 | 69.4 |
| 400 | 73.1 | 58.4 |
| 500 | 93.3 | 13.3 |
| | X _{HC} lean condition /% | X _{CO} lean condition /% |
| 200 | 53.6 | 100 |
| 300 | 82.6 | 98.2 |
| 400 | 93.4 | 97.0 |
| 500 | 96.7 | 96.9 |

Next, studies of Pt/Rh-MgO-Al₂O₃ catalyst in conditions of cyclic changes (rich/lean: 30/30; 30/60; 30/90), in temperature range 200-500°C were performed. Two gas flow rates – 2 dm³/min (SV=3000 h⁻¹) and 5 dm³/min (SV=7000 h⁻¹) were used. On the basis of the results of these studies, NO_x conversion during different cyclic mixture changes was calculated.

In all cases the highest NO_x conversion was observed at 200°C. During combustion of rich fuel mixture at SV=3000 h⁻¹ and SV=7000 h⁻¹ conversion decreased while the temperature increased, however, it maintained between 80-100 %. It should be noted that the growth of NO_x conversion was observed in the low flow rate (SV=3000 h⁻¹) for 30/30 and 30/60 cycles at 400°C (Fig. 3a and 3b) while in the high flow rate (SV=7000 h⁻¹) the growth was observed at 500°C (Fig. 4b and 4c).

For lean fuel mixture NO_x conversion decreased with temperature growth. At SV=7000 h⁻¹ (Fig. 4) the decrease of NO_x conversion was more rapid than at SV=3000 h⁻¹ (Fig.3). These

differences could be caused by different time of gas presence in the reactor (different time reactions of each component of catalyst and gases). During 30/30 cyclic changes of mixture (Fig. 3a and 4a) the decrease to 50-55 % was observed but curves illustrating this fall had different character above 300°C at SV=3000 and 7000 h⁻¹. Similar differences for 30/60 cycle have been observed (Fig. 3b and 4b).

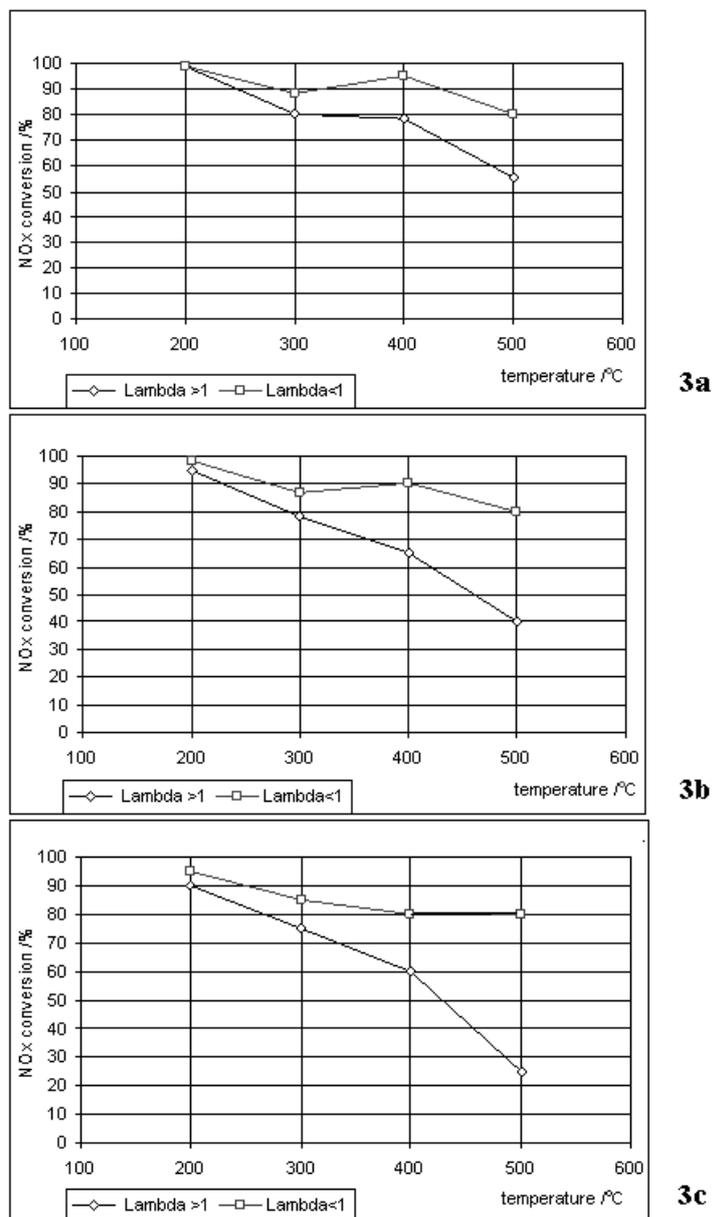


Fig. 3 Nitrogen oxides average conversion ratio as a function of temperature (for different cycles-rich/lean 30/30- **3a**; 30/60- **3b** and 30/90- **3c**) over Pt/Rh-MgO-Al₂O₃ catalyst. Gas flow rate 2 dm³/min (SV=3000 h⁻¹).

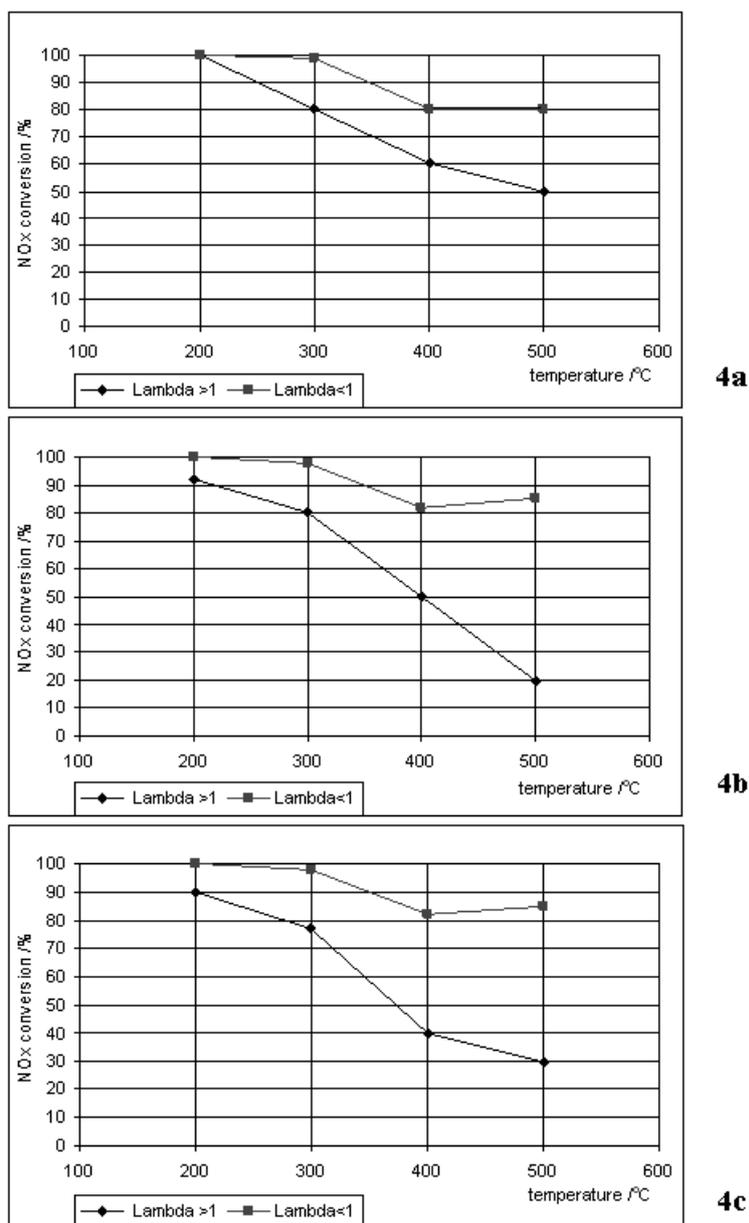


Fig. 4 Nitrogen oxides average conversion ratio as a function of temperature (for different cycles-rich/lean 30/30- **4a**; 30/60- **4b** and 30/90- **4c**) over Pt/Rh-MgO-Al₂O₃ catalyst. Gas flow rate 5 dm³/min (SV=7000 h⁻¹).

To study NO_x storage ability, the bed reactor Pt/Rh-MgO-Al₂O₃ was tested in lean fuel mixture to reach a steady state of NO_x conversion (the level on which only selective catalytic reduction of NO_x - NO_x-SCR takes place). The measurements took place in the following conditions: gas flow rate 2 dm³/min (SV=3000 h⁻¹) or 5 dm³/min (SV=7000 h⁻¹) and temperature range between 200-500°C. Figure 5 presents changes of maximal and minimal NO_x conversion and time of NO_x storage as temperature function (for SV=3000 h⁻¹-Fig. 5a; SV=7000 h⁻¹-Fig. 5b). At lower space velocity gradual decrease of NO_x conversion and time of NO_x storage were observed (Fig. 5a) whereas at SV=7000 h⁻¹, NO_x conversion decreased to similar level. Above 300°C the process happened to be more rapid even though the time of NO_x storage increased above 300°C.

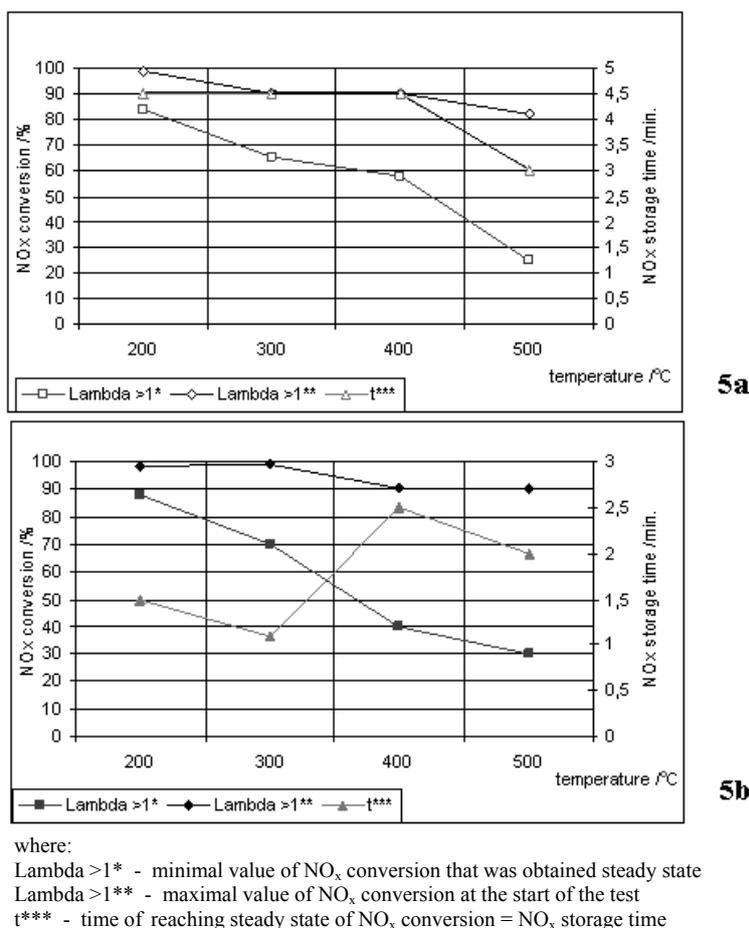


Fig. 5 Maximal and minimal NO_x conversion for lean condition and time of NO_x storage as a function of temperature over Pt/Rh-MgO-Al₂O₃ catalyst. Gas flow rate 2 dm³/min (SV=3000 h⁻¹)- **5a**; 5 dm³/min- **5b** (SV=7000 h⁻¹).

3.2. Activity of the monolith reactor

Catalytic reactor Pt/Rh-MgO/CeO₂/Al₂O₃, prepared on the steel monolith, was tested at temperature of 200°C and 300°C for gas flow rate 2 dm³/min (SV=3500 h⁻¹) and 5 dm³/min (SV=9000 h⁻¹). The results are presented in table 3 and in Fig. 6.

Degrees of NO_x conversion for Pt/Rh-MgO/CeO₂/Al₂O₃ catalyst were much lower than for bed reactor Pt/Rh-MgO/Al₂O₃; especially during lean fuel mixture combustion. The NO_x conversion decreases even to 20% at such a low temperature level as 300°C. For the space velocity SV=3500 h⁻¹ and rich fuel mixture, NO_x conversion was at the level of 85-98 % but for lean fuel mixture it was at a wide range of 23 to 70 %. When SV was increased to 9000 h⁻¹, decrease of NO_x conversion with longer lean fuel mixture period was observed. It could be caused by the decrease of the catalyst ability to NO_x storage and to regenerate during rich fuel mixture combustion.

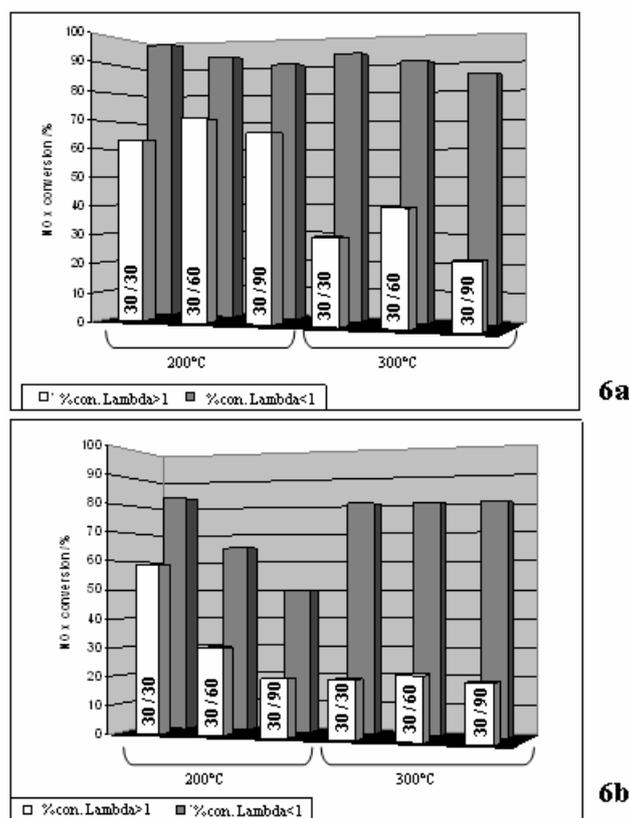


Fig. 6 The average nitrogen oxides conversion ratio for different exhaust composition and cycles (rich/lean mixture - 30/30, 30/60, 30/90) over Pt/Rh-MgO/CeO₂-Al₂O₃ reactor (SV=3500 h⁻¹- 6a; SV=9000 h⁻¹- 6b).

4. Conclusions

The prepared bed reactor containing magnesia as NO_x trap oxidizes CO and HC and reduces NO_x during cyclic changes of air to fuel mixtures. Oxidation and reduction properties of the reactor are strongly dependent on the cycle of mixture changes and temperature. Generally there is an average NO_x conversion ratio decrease with the increase of lean period time. The highest NO_x conversion was obtained for cycle of 30 s ($\lambda=1.19$) + 30 s ($\lambda=0.95$) and space velocity SV=3000 h⁻¹. During the work on only lean fuel mixture the best results were obtained at 200-300°C for SV=3000 h⁻¹, when NO_x conversion was in the range between 65-100 % and the time of NO_x storage was 4.5 minutes.

For monolith type of reactor Pt/Rh-MgO/CeO₂-Al₂O₃ conversion didn't obtain acceptable results above 200°C for both SV values. Probably it is connected with much lower specific surface area in comparison with bed reactor Pt/Rh-MgO-Al₂O₃ therefore modification of this catalyst should be done.

The relation of the surface area to the volume of the reactor was higher for the monolith reactor than for the bed type but the specific surface area was 10 times lower than level for the bed reactor. To obtain better results extended specific surface area of the ceramic layer on monolith catalyst is necessary.

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