Acta Geodyn. Geomater., Vol. 11, No. 2 (174), 175–186, 2014
DOI: 10.13168/AGG.2013.0063

journal homepage: http://www.irsm.cas.cz/acta

REVIEW

# A SHORT REVIEW ABOUT $NO_X$ STORAGE/REDUCTION CATALYSTS BASED ON METAL OXIDES AND HYDROTALCITE-TYPE ANIONIC CLAYS

**Magdalena JABŁOŃSKA [1], Antonio Eduardo PALOMARES GIMENO [2] *,**
**Agnieszka WĘGRZYN [1] and Lucjan CHMIELARZ [1]**

[1] *Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland, Phone 12 6336377, Fax 12 6340515*
[2] *Instituto de Tecnologia Quimica, UPV-CSIC, Universidad Politecnica de Valencia, Avenida de los Naranjos s/n, 46022 Valencia, Spain;*
*Departmento de Ingeniería Química y Nuclear, Universidad Politecnica Valencia, Avda. de los Naranjos s/n, 46022 Valencia, Spain*
Phone: 34 963877000, Fax: 34 963879009

**Corresponding author's e-mail:* apalomar@iqn.upv.es

ARTICLE INFO

***Article history:***
Received 7 March 2013
Accepted 11 November 2013
Available online 20 December 2013

***Keywords:***
$NO_x$
Storage/reduction catalyst
Metal oxides
Hydrotalcite based catalysts

ABSTRACT

The increasing problem of atmospheric pollution by $NO_x$ has resulted in stricter regulations on their emissions. $NO_x$ storage/reduction (NSR) is considered as efficient catalytic technology to abate lean-burn $NO_x$. A wide variety of catalysts have been extensively examined for this purpose. The use of metal oxides, hydrotalcites and their derivatives as $NO_x$ storage/reduction catalysts has been reviewed. Suitable combination particularly the catalytic redox component and the storage component can lead to improved activity in $NO_x$ decomposition and capturing under the lean-rich conditions.

## 1. INTRODUCTION

The negative impact on atmosphere, environment and human health caused by $NO_x$ (NO, $NO_2$), led to development a variety of technologies responsible for the control of nitrogen oxides emissions. Nowadays, the $NO_x$ exhaust after treatment systems include: (i) exhaust gas recirculation (EGR), (ii) selective catalytic reduction (SCR) utilizing anhydrous ammonia or aqueous urea injection, (iii) direct decomposition of NO, (vi) steady-state selective catalytic reduction with hydrocarbons (HC-SCR) under lean conditions, (v) periodic HC-SCR using a $NO_x$ storage and reduction (NSR) catalysts (Kabin et al., 2004). Among them, the $NO_x$ storage/reduction (NSR) technology is currently regarded as a commercially viable solution for the control of $NO_x$ emissions from lean-burn gasoline vehicles. Periodic switches between lean and rich conditions are utilized to achieve control of $NO_x$ emissions (Takahashi et al., 1996; Matsumoto et al., 2000). The prototypical NSR catalysts – Pt (1.0 wt.%)/Ba (15.0 wt.%)/$Al_2O_3$, consist of Pt and BaO dispersed on a high surface area alumina support (Epling et al., 2004). Such catalyst works in two steps: (i) under lean conditions, NO is oxidized into $NO_2$ on the Pt active sites, and $NO_2$ is adsorbed on BaO as nitrate, (ii) under rich conditions, nitrates decompose and $NO_2$ formed is reduced into $N_2$ with HC, CO and $H_2$ present in the exhaust gases (Palomares et al., 2008). The possible mechanism of $NO_x$ storage/reduction in the presence of typical Pt/Ba/$Al_2O_3$ catalysts is presented in Figure 1.

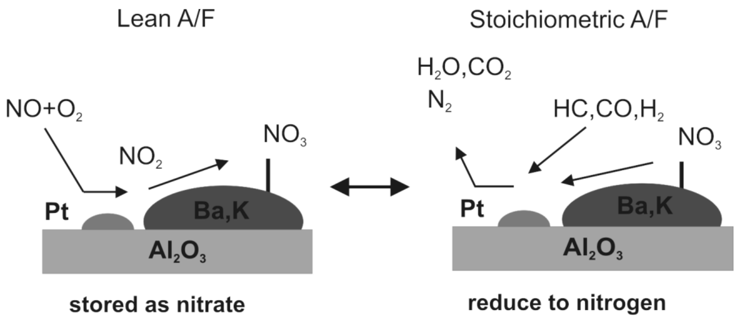

**Fig. 1** The mechanism of NO storage in exhaust gas from lean mixture combustion and their reduction in exhaust gas from rich mixture combustion; symbols: Pt - platinum crystallite, Ba, K - $NO_x$ storing component (Kanazawa, 2004).

The $Pt/Ba/Al_2O_3$ system is the first generation NSR catalyst and efficient control of $NO_x$ emission was achieved in the presence of this catalyst. However, sulfur poisoning, thermal degradation and carbon deposition affect the application of this NSR catalyst. Most of the published studies have examined the Pt/Ba catalysts over a fairly range of the operating conditions, and very few of these reports have comprehensively studied the effect of operating conditions on the NSR catalysts (Lietti et al., 2001; Fridell et al., 1999). The early literature reports were focused on different performance characteristic of the NSR catalytic systems, including the effect of the operating conditions, such as the composition and temperature of the exhaust and the length of the lean/rich cycles (Fridell et al., 1999; Mahzoul et al., 1999).

The development of low-cost, highly efficient and durable NSR catalysts is essential to meet the more stringent $NO_x$ emission standards and realize broad implementation of this NSR technology. In this work, the NSR catalysts based on mixed oxides and hydrotalcites based catalysts are reviewed. Moreover, the major conclusions and some research directions are presented.

## 2. CATALYST FOR $NO_X$ STORAGE/REDUCTION

NSR catalysts are typically composed of alkaline or alkali Earth oxides and noble metal component (Palomares et al., 2008). The alkalinity determines the $NO_x$ trap performance in the following order: K > Ba > Sr > Na > Ca > Li (Kobayashi et al., 1997). For this reason, potassium or barium-based catalysts are studied extensively for their $NO_x$ storage capacity (Takeuchi and Matsumoto, 2004). Pt, Pd and/or Rh are the most widely used noble metals in the NSR catalysts (Liu and Gao, 2011). Combination of merits of basic oxides, noble metals and supports for the $NO_x$ storage/reduction reactions lead to the formulation of metal oxide supports, ion-exchanged zeolites, perovskites as well as hydrotalcites and hydrotalcite based catalysts. Zeolites and perovskites are the starring materials candidatures that show high potential as alternative NSR catalysts. However, they are liable to be deactivated dramatically by $SO_2$ in the exhaust, even at trace amounts, because of the irreversible adsorption of $SO_2$ under both lean-burn and rich-burn conditions (Huang et al., 2001a; Nakatsuji et al., 1999). These disadvantages together, with the high expense of noble metal, demand the further search for cheap and $SO_2$-tolerant NSR catalysts with comparable or better performance for NSR.

### *2.1. METAL OXIDE SUPPORTS*

In the early literature the $Pt/Ba/Al_2O_3$ system was studied to optimize the composition of the catalyst (Lietti et al., 2001; Amberntsson et al., 2003). The obtained results showed that the $NO_x$ adsorption achieved at 300 °C over Pt (1.0 wt.%) / Ba (10.0 wt.%) / $Al_2O_3$ was higher (0.700 mmol(NO)/g) compared to the result obtained with Pt (1.0 wt.%) / Ba(20.0 wt.%)/$Al_2O_3$ (0.581 mmol(NO)/g). However, the amount of $NO_x$ stored on the catalysts in terms of available surface area was much higher in case of the smallest amount of Ba (Lietti et al., 2001). Further research was carried out on the $Pt/Ba/Al_2O_3$ catalysts with different loading of Ba (10.0-20.0 wt.%) and Pt (0.0-2.0 wt.%) (Laurent et al., 2003). Storage capacities increased from 0.260 to 0.320 mmol (NO)/g, when the Pt content increased from 1.0 to 2.0 wt.%. The Pt (1.0 wt.%) / Ba (10.0 wt.%) / $Al_2O_3$ catalysts exhibited the highest $NO_x$ storage capacity (3.500 mol(NO)/g). Moreover, it was shown that the $Pt/Ba/Al_2O_3$ catalysts containing 15.0 or 20.0 % of Ba, exhibited the same storage capacity (3.000 mmol (NO)/g). Finally, it was reported that the optimum $Pt/Ba/Al_2O_3$ catalysts had a composition between 1.25-1.50 wt.% Pt and 15.0-25.0 wt.% Ba (Hendershot et al., 2007). The average initial $NO_x$ storage/reduction for the Pt (1.0 wt.%) / $Al_2O_3$ catalyst was 0.0011 mmol $NO_x$ compared to 0.0377 mmol $NO_x$ obtained for the Pt (1.0 wt.%) / Ba (15.0 wt.%) / $Al_2O_3$, by using $C_2H_4$ as the reducing agent (0.0176 mmol $NO_x$ for reaction conditions containing CO).

In similar line, the performance of a model Pt (2.2 wt.%) / Ba (16.3 wt.%) / $Al_2O_3$ washcoat monolith catalysts for $NO_x$ storage and reduction was analyzed (Kabin et al., 2004). Authors determined the reductant ($C_3H_6$) feed protocol needed to achieve high efficiency of the $NO_x$ removal. The $NO_x$ conversion achieved maximum (60 %) at an intermediate temperature (240 °C). High $NO_x$ conversion under rich conditions using propylene as a reductant was reported also by other researches (Takahashi et al., 1996; Han et al., 2001). The temperature $NO_x$ storage dependence reflects the contribution of kinetic and thermodynamic factors. These uptake data exhibited maximum at an intermediate temperature (250-350 °C). The increase in $NO_x$ storage with exposure time (from the moment until the $NO_x$ effluent concentration was within 2 % of its feed value after exposure of a mixture of 5 % $O_2$ and 500 ppm NO was fed over the catalysts) at a fixed temperature was observed. For shorter exposure the $NO_x$ storage was nearly independent on temperature for a wide range of temperatures. The $NO_x$ storage for the Pt/Ba/alumina monolith fresh catalysts was 0.500 mmol(NO)/g at 480 seconds exposure at 300-350 °C. Further studies revealed, that the maximum conversion of $NO_x$ over the $Pt/Ba/Al_2O_3$ catalyst was observed at 300-400 °C (Centi et al., 2003). Mean $NO_x$ conversion at 300 °C during the lean period (in a sequence of 20 lean-rich composition cycles) for Pt (1.0 wt.%)/Ba (15.0 wt.%)/$Al_2O_3$ was about 95 % compared to 70 % achieved at 500 °C.

Further research on the NSR catalyst concern a systematic investigation of the effect on $NO_x$ storage in model Pt (2.0 wt.%)/Ba (20.0 wt.%)/$Al_2O_3$, Ba (20.0 wt.%)/$Al_2O_3$, Pt (2.0 wt.%)-Rh (1.0 wt.%)/$Al_2O_3$ and Pt (2.0 wt.%)-Rh (1.0 wt.%)(20.0 wt.%)/Ba/$Al_2O_3$ catalysts (Fridell et al., 1999). Significant amounts of $NO_x$ were stored over the catalysts containing both noble metals and barium oxide. Moreover, maximum $NO_x$ storage was observed at about 380 °C (0.022 mmol, when using NO in the feed gas). Around this temperature any significant differences between NO and $NO_2$ storage capacity were observed. In similar line, the $NO_x$ storage/reduction activity between Pt (3.0 wt.%)/Ba (20.0 wt.%)/$Al_2O_3$ and Pd (3.0 wt.%)/Ba (20.0 wt.%)/$Al_2O_3$ were compared using lean-burn exhaust containing NO, $O_2$, $C_2H_6$ and $N_2$ (Salasc et. al., 2002). At 300 °C, the Pd-containing sample showed a higher $NO_x$ storage capacity than Pt-based counterpart (0.029 and 0.016 mol $NO_x$ per mole Ba, respectively). However, at 400 °C, the Pd/Ba/$Al_2O_3$ catalyst was found to exhibit greater low temperature of the $NO_x$ storage capacity than Pt/Ba/$Al_2O_3$ (0.031 and 0.033 mole $NO_x$ per mole Ba, respectively). Authors explained the differences between Pt- and Pd/BaO/$Al_2O_3$ catalysts: at 300 °C by an incomplete NO reduction during the rich phase for the Pt-based catalysts, which suggested poisoning of Pt-sites by adsorbed species; at 400 °C by the lower NO oxidation activity of the supported Pd catalyst. Similar results were obtained at relatively low temperatures (250-350 °C) when hydrocarbons were used as reducing agents (Su et al., 2007). The Pd (1.0 wt.%)/Ba (20.0 wt.%)/$Al_2O_3$ catalyst exhibited about 40 % overall $NO_x$ reduction activity at 300 °C compared to about 12 % obtained using Pt (1.0 wt.%)/Ba (20.0 wt.%)/$Al_2O_3$.

In further investigations, the catalysts containing: Pt, Rh, Ba and La supported on washcoat base, and the catalysts with various loading of Pt (0.00-1.47 wt.%) and Ba (three levels: standard, high, low) were reported (Mahzoul et al., 1999). The obtained results showed that a higher Ba content or/and the presence of Pt in the catalysts increased the storage capacity, which is in agreement with the results obtained by other authors (Takahashi et al., 1996; Sakamoto et al., 1999; Yamazaki et al., 2001). The lack of Rh and La decreased the NO storage amount. In particular, catalysts Pt-Rh-La/Ba/washcoat exhibited 0.530 mmol(NO)/g at saturation at 300 °C. Moreover, the Rh/Ba/$Al_2O_3$ catalysts were reported to exhibit the highest $NO_x$ reduction activity among Pt-, Pd- and Rh-based catalysts (Breen et al., 2008; Abdulhamid et al., 2006). However, the total $NO_x$ conversion on the Rh/Ba/$Al_2O_3$ catalysts was lower than that the other two metal-based NSR catalysts. The low NSR activity of Rh/Ba/$Al_2O_3$ was due to its low $NO_x$ storage capacity. The activity of the catalysts (%$NO_x$ stored as a function of cycle duration - 60 s lean/1.2 s rich cycles with 1.5 % $H_2$ + 4.5 % CO reductant mixure at 350 °C) was found to be presented in the following order (Breen et al., 2008):

Pt(1.6 wt.%)/Ba(17.5 wt.%)/$Al_2O_3$ >

Pt(0.5 wt.%)-Rh(0.8 wt.%)/Ba(17.5 wt.%)/$Al_2O_3$>

Rh(1.1 wt.%)/Ba(17.5 wt.%)/$Al_2O_3$ >

Pt(0.5 wt.%)/Ba(17.5 wt.%)/$Al_2O_3$

Further studies confirmed lower $NO_x$ trapping capacity and NO oxidation activity for Pt-Rh/Ba/$Al_2O_3$ compared to the Pt/Ba/$Al_2O_3$ catalyst (Amberntsson et al., 2002; Amberntsson et al., 2003). For example, $NO_x$ storage (mole NO/mole BaO) at 400 °C for Pt (4.0 wt.%)/Ba (13.0 wt.%)/$Al_2O_3$ was 0.116 related to 0.061 achieved for Pt (2.0 wt.%)-Rh (1.0 wt.%)/Ba (13.0 wt.%)/$Al_2O_3$ catalyst. Nevertheless, $NO_x$ reduction activity over the Pt-Rh/Ba/$Al_2O_3$ catalysts was better than that for the Pt/Ba/$Al_2O_3$ catalysts. Due to a higher $NO_x$ reduction activity on Rh regardless of sulfur poisoning, the bimetallic (Pt and Rh) NSR catalysts displayed better $NO_x$ storage/reduction performance than the Pt/Ba/$Al_2O_3$ catalysts.

### *2.1.1. TRANSITION METAL – DOPED CATALYSTS*

The effect of the transition metals addition (e.g. Co, Ni, Cu, Fe) to the Pt/$Al_2O_3$ or Pt/Ba/$Al_2O_3$ system was also reported in the scientific literature (e.g. Centi et al., 2003; Yamazaki et al., 2001; Sakamoto et al., 1999; Hendershot et al., 2003). It was found that the addition of Cu (4.0 wt.%) to the Pt (1.0 wt.%)/Ba (15.0 wt.%)/$Al_2O_3$ catalysts decreased its activity, e.g. at 300 °C the $NO_x$ mean conversion for Pt-Cu/Ba/$Al_2O_3$ was about 60 % compared to around 95 % achieved for the Pt/Ba/$Al_2O_3$ catalyst (Centi et al., 2003). Similar results were reported even earlier (Yamazaki et al., 2001). The addition of Cu (10.6 wt.%) to the fresh NSR catalysts Pt(1.67 wt.%)/Ba(34.3 wt.%)/$Al_2O_3$ or Pt(1.67 wt.%)/$Al_2O_3$, decreased $NO_x$ conversion at studied temperature (250-350 °C). In similar line, the effect of the addition of: Ni, Fe or Co to Pt (1.67 wt.%)/$Al_2O_3$ or Pt (1.67 wt.%)/Ba(34.3 wt.%)/$Al_2O_3$ was investigated. The $NO_x$ conversions over the fresh Fe-(9.3 wt.%), Co-(9.8 wt.%), and Ni-(9.8 wt.%) based catalysts with or without the Ba-compound, were nearly equal to that of the fresh Pt/Ba/$Al_2O_3$ catalyst and nearly equal or even slightly higher than that of the fresh Pt/$Al_2O_3$ ~~catalysts~~ at every tested temperature, respectively. In addition, it was reported that introduction of Fe (1.1 wt.%) to the Pt(3.7 wt.%)/$Al_2O_3$ catalysts had not significant effect in the reactivity of Pt on the Pt/Fe/$Al_2O_3$ catalysts after being heated in flow of 7.5 % $O_2/N_2$ (Sakamoto et al., 1999). The iron loading was found to have a much smaller effect than Pt and Ba on the performance of NSR catalysts (Hendershot et al., 2007). However, in another report a crucial role of iron on the $NO_x$ storage capacity by comparing Pt (1.5 wt.%) / Ba (26.3 wt.%) / $Al_2O_3$ and Pt

(1.5 wt.%)/Fe(11.0 wt.%)/Ba(28.0 wt.%)/$Al_2O_3$ was found (Hendershot et al., 2003). The later exhibited much lower amounts of stored $NO_x$ than the former at temperatures above 250 °C.

Further investigation on Fe introduced to the Ba/$Al_2O_3$ structure was performed (Luo et al., 2008). It was observed, that after introduction of Fe (7.6 wt.%) to Ba (15.0 wt.%)/$Al_2O_3$ prepared by two-step wet impregnation method, the $NO_x$ storage capacity efficiency increased by 26 % from 0.186 to 0.226 mmol/g at 300 °C. This results indicated that $Fe_2O_3$ had a positive effect on the $NO_x$ storage. The fresh Pt (1.5 wt.%)-promoted catalysts displayed similar storage profiles comparing to Ba/$Al_2O_3$ and Fe-Ba/$Al_2O_3$. After reduction pretreatment (under pure hydrogen at 500 °C for 1 h) of the Pt-Fe/Ba/$Al_2O_3$ sample the $NO_x$ storage capacity slightly decreased (from 0.245 to 0.239 mmol/g). Positive effect of Fe (2.5 wt.%) addition to Pt (1.0 wt.%) / Ba (15.0 wt.%) / $Al_2O_3$ or Ba (15.0 wt.%)/$Al_2O_3$ catalysts on $NO_x$ storage/reduction efficiency was also investigated (Vijay et al., 2005). Additionally, the effect of Mn (2.5 wt.%) or Co (2.5 wt.%) addition to the catalysts was derived. Under fuel lean conditions, the addition of Mn or Fe slightly improved the $NO_x$ storage, whereas deposition of Co more than doubled the $NO_x$ storage. The Co(5.0 wt.%)/Ba(15.0 wt.%)/$Al_2O_3$ catalysts was found to store $NO_x$ (0.030 mmol) as efficiently as Pt (1.0 wt.%) / Ba (15.0 wt.%) / $Al_2O_3$. The Pt (1.0 wt.%)/Co(5.0 wt.%)/Ba(15.0 wt.%) catalysts demonstrated excellent $NO_x$ storage (0.067 mmol). Moreover, Co exhibited a comparable ability as Pt to oxidize NO under lean conditions, which clarifies the application of easily accessible and low cost transition metal catalyst (Vijay et al., 2006). Further confirmation by XAFS measurement revealed that the active phase of Co was cobalt(II, III) oxide ($Co_3O_4$) (Park et al., 2007a). It was proposed that $Co_3O_4$ has the ability to store $NO_x$ in the form of nitrite, nitrate and other complex N-containing species (Kantcheva and Vakkasoglu, 2004).

Studies of the Co-based Pt/Ba/$Al_2O_3$ system was also reported (Vijay et al., 2005). The Pt (1.0 wt.%) /Co (5.0 wt.%)/Ba (20.0 wt.%)/$Al_2O_3$ catalyst was found to possess the largest $NO_x$ storage capacity within the temperature range of 200-350 °C (0.883 mmol(NO)/g at 300 °C) (Wang et al., 2010). The studies revealed that the addition of Co accelerated the formation nitrites/nitrates on Ba sites and also improved $NO_x$ adsorption on Al sites. The close contact of Co with Ba/Al proved more active sites for NO adsorption, oxidation and desorption. Moreover, the synergetic effect of Pt and Co could accelerate the $NO_x$ reduction.

There are also interesting studies focused on introduction Pt as oxidizing agent and Rh as reducing agent (Gill et al., 2004). A statistical design of experiments approach to further explore the impact of Co on the performance of Pt (1.0 wt.%) / Ba (15.0 wt.%) / $Al_2O_3$ and Rh (1.0 wt.%) / Ba (15.0 wt.%)/$Al_2O_3$ catalysts under a broad variety of fuel-lean/rich cycles were used (Vijay et al., 2006). The addition of Co(5.0 wt.%) increased the $NO_x$ storage capacity of Rh/Ba/$Al_2O_3$ and Pt/Ba/$Al_2O_3$ catalysts by 50 and 100 % under long-cycling conditions, respectively. The performance of the Co-Pt/Ba/$Al_2O_3$ catalysts in terms of total $NO_x$ storage achieved 0.450 mmol/g at 375 °C. Moreover, the Co- and Pt/Rh-containing catalyst showed 70-75 % $NO_x$ conversion in short-cycle studies, under the same operating conditions. These studies revealed that the reduction capacity of Co was not comparable to that of Pt or Rh. Noble metals were still required for catalyst regeneration in the rich conditions.

#### *2.1.2. ALKALI/ALKALINE-EARTH OXIDE – DOPED CATALYSTS*

The advanced studies considered partially or totally replacement Ba by other metals of the beryllium group (e.g. Mg, Ca, Sr). For example, the $NO_x$ storage/release performance on Ba/$Al_2O_3$, Sr/$Al_2O_3$, Ca/$Al_2O_3$ or Mg/$Al_2O_3$ were studied (Kustov and Makkee, 2009). The obtained results indicated that most of the storage component did not participate in nitrates storage. The storage capacity at 300-450 °C increased from Ba/(5.7 wt.%), to Sr/(16.5 wt.%) and to Ca/$Al_2O_3$ (24.9 wt.%) catalysts, which was related with the difference in the availability of the storage component. The storage capacity obtained for the Mg-based system was quite low (6.1 wt.%) perhaps due to the fact that most of the stored nitrates was decomposed under storage conditions (200 °C). Further modification of the Ba-based storage components into a Ba-Mg/Ca-based composite of the Pt(1.0 wt.%)/Ba(17.0 wt.%)/$Al_2O_3$ sample also was investigated (Basile et al., 2006; Basile et al., 2007). The Toyota-type catalysts exhibited NO conversion higher than 90 % at temperatures of 200-300 °C. When Ba was replaced by Ca(5.0 wt.%), the conversion remained significantly lower than that of the model catalyst; furthermore, any activity below 150 °C was registered. The Pt (1.0 wt.%)/Mg (3.0 wt.%)/$Al_2O_3$ catalyst exhibited an intermediated activity between those of the Pt/Ba/$Al_2O_3$ sample at temperatures 200-300 °C, although associated with a complete absence of aktivity at 500 °C. The Pt (1.0 wt.%) / Ba (8.5 wt.%)-Mg (1.5 wt.%) / $Al_2O_3$ catalysts exhibited a very good activity at low temperature (≤200 °C), while at 250 °C the activity was only slightly lower compared to the Pt/Ba/$Al_2O_3$ catalysts. Furthermore, at high temperature (≤350 °C), this catalysts exhibited greater activity than the reference catalysts. The trend was reversed at higher temperatures (300-400 °C). Therefore, the optimization of Ba and Mg composition in the NSR catalysts can be important in order to obtain better $NO_x$ capacity at a wide temperature window.

Meanwhile, the co-impregnated Ba-Mg system exhibited high resistance for deactivation by $SO_2$.

In the next step, the promoting role of noble metals (Pt, Rh, Pd) on alkaline earth metal oxide-based $NO_x$ storage catalysts under lean-burn conditions was studied (Huang et al., 2001a). The NO adsorption efficiency on each catalyst (in 450 s) at 300 °C was found to increase in the order of:

Ca(5.0 wt.%)/$Al_2O_3$(0.052 mmol/g) <

Pd(1.0 wt.%)/Ca(5.0 wt.%)/$Al_2O_3$ (0.097 mmol/g) <

Pt(1.0 wt.%)/Ca(5.0 wt.%)/$Al_2O_3$ (0.180 mmol/g) <

Rh(1.0 wt.%)/Ca(5.0 wt.%)/$Al_2O_3$ (0.280 mmol/g).

The authors claimed that the addition of Rh provided better $NO_x$ storage ability for a series of the Ca/$Al_2O_3$ catalysts, compared to Pt, due to more effective $NO_2$ formation. This statement, however, was contradicted by several studies on the $Al_2O_3$-supported Pt and/or Rh catalysts. For example, the same activity for NO oxidation over Rh/$Al_2O_3$ and Pt/$Al_2O_3$ was reported (Kobayashi et al., 1997). It was shown that in the presence of the Rh (2.0 wt.%)/$Al_2O_3$ catalyst not more than 30 % of inlet NO is oxidized to $NO_2$ in the presence of $C_3H_6$ at 400 °C. The Pt-counterpart catalysts in all cases were reported to provide higher amounts of $NO_2$ compared to the Rh-based catalysts (Efthimiadis et al., 1998; Efthimiadis et al., 1999; Toubeli et al., 2000).

Apart from the above discussed alkaline earth metals, alkali metals such as K, was also extensively studied as a $NO_x$ storage component for the NSR catalysts. Potassium gained attention as a storage phase, instead of or together with Ba. It was shown that co-loading of $K_2O$ with BaO enhanced the thermal stability of stored $NO_x$. In addition, the combination of oxides after hydrothermal treatment preserved their storage capacity better than Ba/$Al_2O_3$ (Park et al., 2007b). Additionally, a beneficial influence of K over Ba with respect to the $NO_x$ storage capacity was reported over the flame synthesized Pt (1.0 wt.%) / K (5.8 wt.%)/$Al_2O_3$ catalysts, which were found to achieve over 80 % $NO_x$ conversion in the temperature range of 300-400 °C (Büchel et al., 2009). Moreover, the results obtained over the Pt (1.0 wt%) / K (4.5 wt%) / $Al_2O_3$ catalysts revealed that there are able to stored up to 0.797 mmol(NO)/g at 250 °C within 1 h (Toops et al., 2005; Toops et al., 2006). The Pt(0.07-0.35 g)-K(1.0-3.3 g)/$MgAl_2O_4$ catalysts, in which the spinel ($MgAl_2O_4$) support enhanced the basicity of the K, were used as storage component (Takahashi et al., 2007a). The $NO_x$ storage capacity determined for the fresh and thermally aged K/Pt/$MgAl_2O_4$ catalysts were apparently higher than those obtained for the K/Pt/$Al_2O_3$ catalysts. For example, the relative $NO_x$ storage capacity measured for the fresh Pt (0.07 g)-K (2.0 g)/$MgAl_2O_4$ catalyst was about 4 (a.u) compared to about 2 (a.u) achieved for the fresh Pt (0.07 g)-K (2.0 g)/$Al_2O_3$ sample at 600 °C. In similar line, the Ba- or K-free Pt(1.0 wt.%)/$MgAl_2O_4$ catalyst obtained by single-step flame made also was studied (Roy et al., 2010). The catalysts containing of nano-sized Pt dispersed on $MgAl_2O_4$ showed excellent dynamic performance in $NO_x$ storage-reduction at short regeneration periods (<30 s). The amount of $NO_x$ storage during the rich periods (e.g. 30 s) over Pt/$MgAl_2O_4$ at 350 °C was about 87 % compared to 70 % for the reference Pt (1.0 wt.%) / Ba (20.0 wt.%)/$Al_2O_3$ catalyst. Moreover, the Pt/$MgAl_2O_4$ system exhibited higher thermal stability (up to 800 °C) and lower tolerance for sulfur poisoning.

### *2.1.3. OTHER METAL OXIDE SUPPORTS*

It was presented in the mentioned above examples, that despite of large number of studies devoted to the application of the supported metal oxide catalysts in the $NO_x$ storage/reduction process apart from the Pt/Ba/$Al_2O_3$ Toyota-type catalysts any other catalytic system was up-till-now fully accepted for commercialization. The main reason is very poor sulphur tolerance (Matsumoto et al., 2000; Amberntsson et al., 2003; Efthimiadis et al., 1999). Sulfur poisons the key components of the NSR catalysts (Pt or BaO). Different attempts toward controlling the composition of the NSR catalysts, which can prevent their poisoning by $SO_2$ (Xiao et al., 2008; Yamazaki et al., 2001; Hendershot et al., 2004) were proposed. Studies focused mainly on the modification of the support ($Al_2O_3$) were reported to improve the NSR activity.

The benefit of the Ce-promoted catalysts is sulfur resistance since it is known that $SO_2$ can be stored as cerium sulfate, which may protect the $NO_x$ storage component (e.g. BaO) from sulfur poisoning (Peralta et al., 2006). The sulfur resistance and thermal resistance of $CeO_2$ and $Al_2O_3$ as the supports was compared (Kwak et al., 2008). The Pt (2.0 wt.%) / Ba (10.0 wt.%) / $CeO_2$ sample exhibited slightly higher $NO_x$ uptake compared to Pt (2.0 wt.%)/Ba (20.0 wt.%)/$Al_2O_3$, and the additionally the $CeO_2$-based catalysts showed higher sulfur tolerance than the $Al_2O_3$-based one. The $NO_x$ uptake at 250 °C, obtained for the $CeO_2$-based catalysts was about 60 % which was significantly higher than 49 % measured for the $Al_2O_3$-based catalyst. $NO_x$ uptake of the $SO_2$-treated ceria-based catalysts was reduced to 43 %, while for the alumina-based catalyst $NO_x$ uptake decreased to 23 %. However, it was indicated that Pt (0.74 wt.%)/Ba (15.5 wt.%)/$CeO_2$ exhibited inferior $NO_x$ storage performance, particularly the reduction/regeneration activity compared to the $Al_2O_3$ supported catalysts (Casapu et al., 2008). Authors proposed that the incomplete reduction of stored $NO_x$ species by Pt/Ba/$CeO_2$ was caused by faster and more profound re-oxidation of Pt particles during the lean period.

The Ba(Co,K)/$CeO_2$ system was studied as potential candidate for the $NO_x$ abatement from diesel exhaust (Milt et al., 2003). The $NO_2$ storage capacity of the Ba (16.0 wt.%)/$CeO_2$ sample was 63.1 %, while the $NO_2$ storage capacity of the K (7.0 wt.%) / Ba (16.0 wt.%) / $CeO_2$ sample was 44.7 %. For the Co (12.0 wt.%)-K (7.0 wt.%) / Ba (16.0 wt.%) / $CeO_2$ sample, the solid storage capacity was very small in the presence of NO or NO + $O_2$. However, the $NO_2$ storage capacity of this sample at 300 °C (27.1 %) was comparable to that of Pt/Ba/$Al_2O_3$ (Laurent et al., 2003).

The storage of $NO_x$ under lean conditions for the Pt (0.24 wt.%)-Mn (8.0 wt.%)-K (20.0 wt.%)/$Al_2O_3$-$CeO_2$ (10.0 wt.%) catalysts was studied (Lesage et al., 2007). The ratio between the quantity of $NO_x$ stored during the full $NO_x$ storage period and for the entire experiment was around 46 % at 300 °C and 69 % at 400 °C, compared to 55 % (300 °C) and 98 % (400 °C) obtained for the Pt/Ba/$Al_2O_3$ catalyst (Lietti et al., 2001). However, $NO_x$ storage determined for full catalyst saturation for Pt/Ba/$Al_2O_3$ was 0.324 mmol/g at 400 °C compared to 0.675 mmol/g achieved for the Pt-Mn-K/$Al_2O_3$-$CeO_2$ catalysts. In similar line, the Pt (0.83 wt.%)/Ba (19.1 wt.%)/$Al_2O_3$-$CeO_2$ (20.4 wt.%) and the Pt (0.83 wt.%) / Ba (19.1 wt.%) / $Al_2O_3$-$CeO_2$(20.4 wt.%)-$Fe_2O_3$ (3.3-13.2 wt.%) catalysts were studied (Yamazaki et al., 2004). The fresh Pt/Ba/$Al_2O_3$-$CeO_2$-$Fe_2O_3$ (6.6 wt.%) catalyst showed the same NSR activity as fresh Pt/Ba/$Al_2O_3$-$CeO_2$ when either $C_3H_6$ or CO were used as reducing agents at temperatures from 250 to 350 °C. The $NO_x$ conversion for both the catalysts was about 75 % at 350 °C when $C_3H_6$ was used as ~~a~~ reducing agent. After thermal aging at 850 °C the $NO_x$ conversion for both the catalysts dropped to about 40 %.

$CeO_2$, $ZrO_2$ (Clacens et al., 2004) or $CeO_2$-$ZrO_2$ (Strobel et al., 2006) were tested as an alternative supports of the NSR catalysts. The $CeO_2$-$ZrO_2$ solid solution with 20 mole % of Zr was developed to improve the thermal stability of $CeO_2$ (Ozawa et al., 1991; Ozawa et. al., 1993). In further studies, a series of the Pt/Ba/$Ce_xZr_{1-x}O_2$ (x = 0-1) catalysts, obtained by two-nozzle flame spray pyrolysis method was tested (Strobel et al., 2006). The obtained results revealed that the reduction of Pt at 500 °C in flow of 5 % $H_2$/Ar prior to the catalytic test strongly enhanced the $NO_x$ reduction activity of Pt at lower temperatures and thus increased the $NO_x$ conversion. Even at 300 °C, the prereduced Pt was active for $NO_x$ reduction, resulting in $NO_x$ conversion of 33.6 %. The $H_2$-pretreatment increased also the efficiency of the $NO_x$ reduction for Pt deposited on $ZrO_2$, resulting in $NO_x$ conversion of 52.8 % at 300 °C compared to 10.6% for the as-prepared catalyst.

The influence of both support oxide ($Al_2O_3$, $SiO_2$, $Al_2O_3$-(5.5 wt.%) $SiO_2$, $Ce_{0.7}Zr_{0.3}O_2$) and Ba-loading (5.0-30.0 wt.%) in the Pt/Ba/support model catalysts on sulfur resistance was also studied (Corbos et al., 2008). The Pt / (20.0 wt.%) Ba / $Al_2O_3$-(5.5 wt.%) $SiO_2$ catalyst displayed high $NO_x$ capacity at 300 °C for the fresh (0.022 mmol/g) and sulfated samples (0.011 mmol/g). Moreover, these catalysts, together with Pt/Ba (5.0-10.0 wt.%)/$Ce_{0.7}Zr_{0.3}O_2$ presented lower sensitivity to sulfur with nearly 50 % of their initial $NO_x$ storage capacity drop loss. On the contrary, the Pt/(10.0-20.0 wt.%)/$Al_2O_3$ samples presented high sulfur sensitivity, with almost 70 % of the $NO_x$ storage capacity loss after catalyst sulfation.

Also $TiO_2$ was studied as NSR catalysts. $TiO_2$ is an interesting material due to its high tolerance against sulfur poisoning (Hachisuka et al., 2000; Huang et al., 2001b). Substitution BaO for $TiO_2$ in the catalyst, resulted in improvement of the $NO_x$ storage capacity in absence of $SO_x$. However it must be stressed that the Pt (1.0 wt.%)-Rh (1.0 wt.%)/$TiO_2$ (10.0-30.0 wt.%)/$Al_2O_3$ catalysts was more suitable in the presence of $SO_2$ due to its higher tolerance for this poison. In the presence of $SO_2$ and $H_2O$, the $NO_x$ conversion dropped from 94 to 90 % over the Pt-Rh/$TiO_2$ (20.0 wt.%)/$Al_2O_3$ catalysts at 250 °C. Authors explained these results by lower decomposition temperature of sulfates on the $TiO_2$ surface (Huang et al., 2001b).

$TiO_2$ was used as support for the preparation of a series of Pt (1.0 wt.%)/$M_xO_y$ (10.0 wt. %)/$TiO_2$ catalysts, where M = Li, Na, K, Cs, Sr, Ba or La (Yamamoto et al., 2006). The amount of NO sorbed was increased by adding of base oxides to Pt/$TiO_2$ under both $SO_2$-free or $SO_2$-containing atmospheres. The effect of the additives on the NO sorption capacity was in the following order:

$$K > Na > Cs > La > Sr > Ba > Li$$

The NO sorption capacity was significantly deteriorated in $SO_2$-containing atmosphere for all the catalysts except for Pt/$TiO_2$ and Pt/$Li_2O$/$TiO_2$. Total $NO_x$ storage capacity calculated by assuming NO sorbed as nitrate over Pt-$Li_2O$/$TiO_2$ was 6.690 mmol/g at 300 °C.

Another approach studied in the literature was application of $ZrO_2$-$TiO_2$ mixture as support of the catalysts (Fung and Wang, 1996; Lai et al., 2000). The optimal $TiO_2$/$ZrO_2$ ratio was found to be 2/3 (Takahashi et al., 2007b) and the optimum calcination temperature of the $TiO_2$-$ZrO_2$ support resulting in high $NO_x$ storage capacity and the sulfur resistance determined at 650 °C (Liu et al., 2008a). The significant acidity of binary $TiO_2$-$ZrO_2$ can prevent $SO_2$ adsorption and promote $SO_2$ desorption. Thus, the lean-burn $NO_x$ trap catalysts based on such oxide system show much better sulfur-resistance than the Pt/Ba/$Al_2O_3$ catalysts. The effect of $SO_2$ on the adsorption and desorption properties of NO over $TiO_2$-$ZrO_2$ was studied by Ito et al. (Ito et al., 2007), who showed that a maximum adsorptive NO uptake of (n)$TiO_2$-(1-n)$ZrO_2$ was for n = 0.25-0.5. The studied system was found to be effective for the oxidative adsorption of NO at ambient temperature (about 1.000 mmol/g), as well as thermal $NO_x$ desorption at temperatures below 500 °C in the presence of $SO_2$. $TiO_2$-$ZrO_2$ exhibited stable temperature-swing NO adsorption/desorption cycles in a stream of 0.16 % NO, 10 % $O_2$, 100 ppm $SO_2$ and He balance. By contrast, $Al_2O_3$ exhibited a significant deterioration since sulfate species block the base sites from $NO_x$ adsorption. The tolerance of $TiO_2$-$ZrO_2$ to $SO_2$ was associated with the presence of the weak base sites and instability of sulfate species on the surface.

Further attempts were focused on the introduction of some basic additives. For example, the catalytic Pt/K/$TiO_2$-$ZrO_2$ system (Liu et al., 2008; Zou et al., 2009) received more attention due to its excellent performance in $NO_x$ storage and sulfur resistance. Moreover, the Pt (1.0 wt.%) / K (7.0 wt.%) / $TiO_2$-$ZrO_2$ catalysts promoted with Co (5.0 wt.%) or Ce (5.0 wt.%) were studied (Zou et al., 2009). The Co or Ce addition greatly improved the $NO_x$ storage capacity of Pt/K/($TiO_2$-$ZrO_2$) due to the enhanced oxidation ability and the release of more K sites. The Ce addition induced higher surface K/Ti atomic ratio and larger $NO_x$ storage capacity (0.382 mmol/g) as compared to Co addition (0.255 mmol/g) at 350 °C (0.194 mmol/g for Pt/K/($TiO_2$-$ZrO_2$) catalyst). After sulfation and regeneration, the promoted catalysts showed more or less decreased the $NO_x$ storage capacity efficiency comparing to Pt/K/$TiO_2$-$ZrO_2$ due to the formation of more sulfates, especially for the Co-promoted catalysts. High oxidation ability and high K/Ti ratio of the Ce-promoted catalysts did not reduced the $NO_x$ storage capacity, which was 0.142 mmol/g after sulfation and regeneration.

The mixed oxides containing $Al_2O_3$, $ZrO_2$ and $TiO_2$ were evaluated as a novel support for the NSR catalysts. It was found that the mixture of $TiO_2$ and γ-$Al_2O_3$ used as support could minimize the amount of $SO_x$ deposit on the catalysts (Matsumoto et al., 2000). In similar line, a nano-composite containing $Al_2O_3$ and $ZrO_2$-$TiO_2$ (AZT) solid solution, which was used as support for Pt (1.23 wt.%) / Rh (0.06 wt.%) / Ba (18.8 wt.%) / K (5.8 wt.%) / AZT was synthesized (Imagawa et al., 2007; Imagawa et al., 2009). The amounts of $NO_x$ stored at 400 and 500°C were similar to that obtained at 300°C. The $NO_x$ storage capacity of the thermally aged catalysts containing nano-composite oxide was about 0.038 mmol/g at 400 °C.

In the further studies, the other combinations of mixed metal oxides were also evaluated as supports for the NSR catalysts. For example, the oxidative NO adsorption onto $MnO_x$-$ZrO_2$ at temperature below 200 °C was reported by Eguchi et al. (1996), who showed that the amount of stored NO was the largest for the sample with the Mn/Zr ratio of 1 (0.133 mol/mol-Zr at 200 °C). Due to weaker basicity, the thermal desorption of $NO_x$ took place at temperatures below 400 °C, compared to the Ba-based adsorbents, which needs temperatures up to 600 °C. Also other binary oxides, like $MnO_x$-$CeO_2$ were studied as catalysts for the $NO_x$ storage capacity process (Machida et al., 2003; Qi and Yang, 2003). Binary $MnO_x$ (50.0 wt.%)-$CeO_2$ (50.0 wt.%) oxide, with the fluorite-type structure adsorbed a large amount of NO to yield surface nitrite and/or nitrate (Machida et al., 2000).

Further studies were focused on testing of the MgO (50.0 wt.%)-$CeO_2$ (50.0 wt.%) (Costas and Efstathiou, 2007) or $CeO_2$-$ZrO_2$(20.0 wt.%) / $Al_2O_3$ (64.0 wt.%)-BaO (16.0 wt.%) oxide systems (Liotta et al., 2002). The studies performed for these catalysts showed that $NO_x$ storage was quite comparable with that of the reference Pt (1.0 wt.%) / Ba (15.0 wt.%)/$Al_2O_3$ samples.

### *2.2. HYDROTALCITES AND THEIR DERIVED FORM*

Hydrotalcites, which can be characterized with a schematic representation shown in Figure 2, or hydrotalcites derived mixed oxides received considerable attention in the recent research of alternative NSR catalysts.

First of all, the interesting characteristic of hydrotalcites as $NO_x$ storage-reduction catalysts was the formation of well-dispersed MgO particles which can acts as $NO_x$ storage components. The characteristics of these materials depend on the Mg/Al ratio and the presence of the other elements in the structure (Cavani et al., 1991). Another very important of these materials is possibility of reconstructing the hydrotalcite structure from its calcined form during catalytic reaction (so called memory effect) (Cavani et al., 1991), especially in the presence of the high $H_2O$ and $CO_2$ concentrations typical of emissions from car engines. The memory effect originates from the fact that atoms in the heat-treated HT more or less retain their original positions, making reconstruction of the hydrotalcite structure possible.

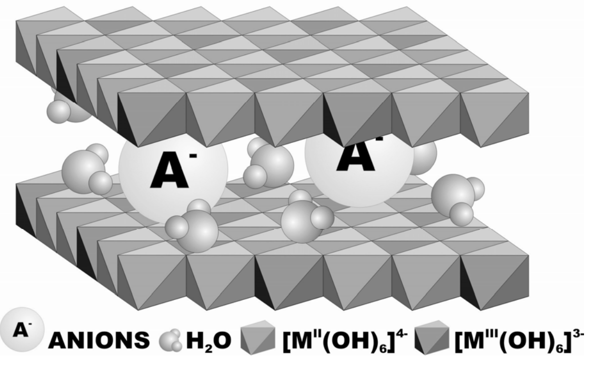

**Fig. 2** Schematic representation of hydrotalcite.

The most often reported NSR catalysts derived from hydrolatcites are noble metal catalysts loaded on Mg(Al)O. Studies based on the Mg/Al structure revealed that the best support for the catalysis of the storage-reduction, comparing the catalysts synthesized with a reference Pt (1.0 wt.%)/Ba (15.0 wt.%)/$Al_2O_3$ Toyota-type, were the Mg/Al hydrotalcite-based catalysts obtained by calcination Mg-Al hydrotalcites at 650 °C (Basile et al., 2004). In this line, $NO_x$ storage-reduction catalysts based on Mg/Al oxide support doped with Pd(1.34 wt.%) were intensively studied (Silletti et al., 2006). The Pd-Mg/Al hydrotalcite based catalyst took up 0.062 mmol(NO)/g in nitrate form at 300 °C. The storage $NO_x$ capacity was much smaller than those reported elsewhere.

It was reported that introduction of small amount of Cu (5.0 wt.%) to the Mg/Al hydrotalcite-like structure to produce the Pd-Cu/Mg/Al oxide catalysts increased NO oxidation rate and slightly improved the storage capacity from 0.157 to 0.175 mmol(NO)/g at 350°C. Similarly, an intensive examination of Mg/Al hydrotalcite based P t(1.0 wt.%) and/or Cu (4.0 wt.%) catalysts for $NO_x$ storage and reduction was done (Fornasari et al., 2002). The hydrotalcite-based Pt-(Cu)-Mg/Al catalysts lead to 80-95 % mean $NO_x$ conversion at 200-300 °C, what is comparable with the activity of the commercial Pt (1.0 wt.%)/Ba (15.0 wt.%)/$Al_2O_3$ catalysts. Moreover, the hydrotalcite-based Pt-Cu catalysts showed higher resistance for $SO_2$ deactivation than the Pt/Ba/$Al_2O_3$ and hydrotalcite-based Pt-catalysts (Centi et al., 2002; Centi et al., 2003; Fornasari et al., 2005.). In fact, Cu-containing hydrotalcite-derived Mg/Al oxides were found to be active and selective catalysts of $NO_x$ removal. Authors mentioned that activity of this material could be promoted by metal alkaline oxides doping. For this reason, the hydrotalcite-derived Pt and Pd catalysts prepared using $CH_3COOK$ and $KNO_3$ as precursors of the storage component were reported (Park et al., 2010). The optimum noble metal ratio was determined to be Pt (0.5 wt.%)/Pd (0.5 wt.%) or Pt (0.25 wt.%)/Pd (0.75 wt.%). Pd was found to be more effective for the high performance of NSR catalysts than Pt, particularly for reducing $NO_x$ at 200°C. Both $CH_3COOK$ and $KNO_3$ were found to be the best K precursors with respect to NSR performance at both low (200 °C) and high (350 °C) temperatures.

The Co/Mg/Al hydrotalcite based catalyst was found to store a high amount of $NO_x$. It was proposed that the obtained oxides effectively catalyzed NO oxidation to nitrites and nitrates that were then stored on the surface Mg/Al oxide (Yu et al., 2006). Co/Mg/Al (20:10:10) and Co/Mg/Al (25:5:10) mixed oxides stored 0.150 mmol(NO)/g at 300 °C, while Mg/Al (30:10) mixed oxide only 0.080 mmol(NO)/g. The introduction of Co into the calcined hydrotalcite significantly enhanced the oxidation of NO to $NO_2$, indicating the occurrence of NO oxidation in some way. It was noted that about 15 and 25 % $NO_x$ was directly decomposed to $N_2$ as well as $N_2O$ over these two catalysts, respectively.

In the further studies, an improvement of NSR catalysts by substitution of $M^{II}$ ($Mg^{2+}$) or $M^{III}$ ($Al^{3+}$) for other cations was reported (Centi et al., 2003; Fornasari et al., 2002; Yu et al., 2007a). Substitution of 50 % $Al^{3+}$ in the Co/Mg/Al (25:5:10) hydrotalcite structure with $Fe^{3+}$, $Mn^{3+}$, $Zr^{4+}$, $La^{3+}$ and testing of such catalysts in $NO_x$ NSR was reported (Yu et al., 2007a). The obtained results showed that $La^{3+}$ enhanced both the storage and reduction of $NO_x$ efficiency. In this system $La_2O_3$ was proposed to link the redox/storage region and lower the activation energies (Yu et al., 2009). To increase the NSR activity, instead of $Mg^{2+}$ cations $Ca^{2+}$ ions were incorporated, what resulted in enhanced alkalinity of the system for nitrite and nitrate storage (Yu et al., 2007b). As a result, Co/Ca/Al (10:20:10) mixed metal oxides stored 0.602 mmol(NO)/g (compared to 0.150 mmol(NO)/g for Co/Mg/Al hydrotalcite and Co/Ca/La/Al (10:20:1:9) hydrotalcite-derived mixed metal oxides 0.634 mmol(NO)/g at 300°C (Yu et al., 2007c; Yu et al., 2009). The Co/Ca/La/Al catalysts directly decomposed 75 % NO to $N_2$ and $O_2$ at 300 °C, while the Co/Ni/Al oxide system decomposed only 50 % of NO.

Further modification of the Co/Ca/La/Al oxide system was based on replacement of some $Ca^{2+}$ cations with more basic $Ba^{2+}$ or $Sn^{2+}$. It was shown that prepared Co/Ca/Ba/La/Al (10:15:5:1:9) and Co/Ca/Sr/La/Al (10:15:5:1:9) mixed oxides influenced activity in NSR and direct decomposition of NO in $O_2$-rich stream (Yu et al., 2007b). The NO storage capacity of the Ba- or Sn-based catalysts was much lower than the Co/Ca/La/Al system. It was explained by the fact that alkalinity of the oxide catalysts was not the only factor determining the NO storage capability. It is also possible that Ba or Sr cations were not well incorporated into the structure due to much larger ionic size.

Advanced studies over the noble metal (Pt, Pd, Ru) or transition metal (V) doped Co/Mg/Al hydrotalcite derived catalysts also were reported (Palomares et al., 2008). Authors studied the combination of redox and the acid-base properties of the Co(Cu)/Mg/Al hydrotalcites in order to design $NO_x$ storage-reduction catalysts stable in the presence of $H_2O$ and $SO_2$. The Co/Mg/Al (16:69:15) catalyst doped with Ru or V(1.0 wt.%) presented a mean NO conversion (after seven lean-rich reaction cycles) of almost 100 % at 300 °C. The mean conversion of 90-95 % at 100 °C was obtained. These catalysts exhibited high conversion even in the presence of $SO_2$ and $H_2O$. In particular the V-promoted catalyst showed a mean NO conversion of 75 % after the seven lean-rich cycles at 300 °C.

Other works over the NSR catalysts focused on the introduction of noble metals in the hydrotalcite structure were performed. The Ru/Mg/Al (1:90:29) mixed oxide derived catalysts exhibited quite high $NO_x$ storage capability of about 0.220 mmol(NO)/g at 350 °C (Li et al., 2007).

In conclusion, catalysts based on noble metals deposited or incorporated into hydrotalcite originated mixed oxides may be considered as promising materials for a new generation of the NSR catalysts. Such catalysts show improved properties with respect to resistance to deactivation by $SO_2$ (Fornasari et al., 2002) and thermal stability (Park et al., 2010). However, further investigation in the presence of real exhaust gases are needed to finally assess the potential of the hydrotalcite as catalysts, catalytic supports or precursors for the NSR process.

## 3. CONCLUSION AND OUTLOOK

In this review, the main developments in the field of the NSR catalyst formulation are presented. Catalysts based on mixed metal oxides and hydrotalcites were presented and discussed.

Hydrotalcite materials, are considered now as one of the most promising catalysts for the NSR process. The development of the material with a new composition (e.g. Co, Mn, Zn, Fe, Ce) can lead to increase the NSR activity, sulfur poisoning resistance and thermal stability.

## REFERENCES

Abdulhamid, H., Fridell, E. and Skoglundh, M.: 2006, The reduction phase in $NO_x$ storage catalysis: Effect of type of precious metal and reducing agent, Appl. Catal. B, 62, No. 3-4, 319–328. DOI: 10.1016/j.apcatb.2005.08.014

Amberntsson, A., Skoglundh, M., Jonsson, M. and Fridell, E.: 2002, Investigations of sulphur deactivation of $NO_x$ storage catalysts: Influence of sulphur carrier and exposure conditions, Catal. Today, 73, No. 3-4, 279–286. DOI: 10.1016/S0920-5861(02)00011-1

Amberntsson, A., Fridell, E. and Skoglundh, M.: 2003, Influence of platinum and rhodium composition on the $NO_x$ storage and sulphur tolerance of a barium based $NO_x$ storage catalyst, Appl. Catal. B, 46, No. 3, 429–439. DOI: 10.1016/S0926-3373(03)00269-8

Basile, F., Fornansatri, G., Livi, M., Tinti, F., Trifiró, F. andVaccari, A.: 2004, Performance of new Pt and Pt-Cu on hydrotalcite-derived materials for $NO_x$ storage/reduction, Top. Catal. 30/31, No. 1-4, 223–227. DOI: 10.1023/B:TOCA.0000029753.61106.ef

Basile, F., Fornansari, G., Grimandi, A., Livi, M. and Vaccari, A.: 2006, Effect of Mg, Ca and Ba on the Pt-catalyst for $NO_x$ storage reduction, Appl. Catal, B, 69, No. 1-2, 58–64. DOI: 10.1016/j.apcatb.2006.05.017

Basile, F., Fornansari, G., Gambatesa, A., Livi, M. and Vaccari, A.: 2007, Reactivity of Mg-Ba catalyst in $NO_x$ storage/reduction, Catal. Today, 119, No. 1-4, 59–63. DOI: 10.1016/j.cattod.2006.08.051

Breen, J.P., Burch, R., Fontaine-Gautrelet, C., Hardacre, C. and Rioche, C.: 2008, Insight into the key aspects of the regeneration process in the $NO_x$ storage reduction (NSR) reaction probed using fast transient kinetics coupled with isotopically labelled $^{15}NO$ over Pt and Rh-containing $Ba/Al_2O_3$ catalysts, Appl. Catal. B, 81, No. 1-2, 150–159. DOI: 10.1016/j.apcatb.2007.12.016

Büchel, R., Strobel, R., Baiker, A. and Pratsinis, S.E.: 2009, Flame-made $Pt/K/Al_2O_3$ for $NO_x$ storage-reduction (NSR) Catalysts, Top. Catal. 52, No. 13-20, 1799–1802. DOI: 10.1007/s11244-009-9334-x

Casapu, M., Grunwaldt, J.-D., Maciejewski, M., Krumeich, F., Baiker, A., Wittrock, M. and Eckhoff, S.: 2008, Comparative study of structural properties and $NO_x$ storage-reduction behavior of $Pt/Ba/CeO_2$ and $Pt/Ba/Al_2O_3$, Appl. Catal. B, 78, No. 3-4, 288–300. DOI: 10.1016/j.apcatb.2007.09.030

Cavani, F., Trifirò, F. and Vaccari, A.: 1991, Hydrotalcite-type anionic clays: Preparation, properties and applications, Catal. Today, 11, No. 2, 173–301. DOI: 10.1016/0920-5861(91)80068-K

Centi, G., Fornansari, G., Gobbi, C., Livi, M., Trifirò, F. and Vaccari, A.: 2002, $NO_x$ storage-reduction catalysts based on hydrotalcite. Effect of Cu in promoting resistance to deactivation, Catal. Today, 73, No. 3-4, 287–296. DOI: 10.1016/S0920-5861(02)00012-3

Centi, G., Arena, G.E. and Perathoner, S.: 2003, Nanostructured catalysts for $NO_x$ storage-reduction and $N_2O$ decomposition, J. Catal., 216, No. 1-2, 443–454. DOI: 10.1016/S0021-9517(02)00072-6

Clacens, J.M., Montiel, R., Kochkar, H., Figueras, F., Guyon, M. and Beziat, J.C.: 2004, Pt-free sulphur resistant $NO_x$ traps, Appl. Catal. B, 53, No. 1, 21–27. DOI: 10.1016/j.apcatb.2004.04.014

Corbos, E.C., Courtois, X., Bion, N., Marecot, P. and Duprez, D.: 2008, Impact of the support oxide and Ba loading on the sulfur resistance and regeneration of Pt/Ba/support catalysts, Appl. Catal. B, 80, No. 1-2, 62–71. DOI: 10.1016/j.apcatb.2007.10.009

Costas, C.N. and Efstathiou, A.M.: 2007, Mechanistic aspects of the $H_2$-SCR of NO on a novel Pt/MgO-$CeO_2$ catalyst, J. Phys. Chem. C, 111, No. 7, 3010–3020. DOI: 10.1021/jp064952o

Efthimiadis, E.A., Lionta, G.D., Christoforou, S.C. and Vasalos, I.A.: 1998, The effect of $CH_4$, $H_2O$ and $SO_2$ on the NO reduction with $C_3H_6$, Catal. Today, 40, No. 1, 15–26. DOI: 10.1016/S0920-5861(97)00113-2

Efthimiadis, E.A., Christoforou, S.C., Nikolopoulos, A.A. and Vasalos, I.A.: 1999, Selective catalytic reduction of NO with $C_3H_6$ over Rh/alumina in the presence and absence of $SO_2$ in the feed, Appl. Catal. B, 22, No. 2, 91–106. DOI: 10.1016/S0926-3373(99)00040-5

Eguchi, K., Watabe, M., Ogata, S. and Arai, H.: 1996, Reversible sorption of nitrogen oxides in Mn-Zr oxide, J. Catal. 158, No. 2, 420–426. DOI: 10.1006/jcat.1996.0043

Epling, W.S., Campbell, L.E., Yezerets, A., Currier, N.W. and Parks, J.E.: 2004, Overview of the fundamental reactions and degradation mechanisms of $NO_x$ storage/reduction catalysts, Catal. Rev. Sci. Eng., 46, No. 2, 163–245. DOI: 10.1081/CR-200031932

Fornasari, G., Trifirò, F., Vaccari, A., Prinetto, F., Ghiotti, G. and Centi, G.: 2002, Novel low temperature $NO_x$ storage-reduction catalysts for diesel light-duty engine emissions based on hydrotalcite compounds, Catal. Today, 75, No. 1-4, 421–429. DOI: 10.1016/S0920-5861(02)00092-5

Fornasari, G., Glöckler, R., Livi, M., Vaccari, A.: 2005, Role of the Mg/Al atomic ratio in hydrotalcite-based catalysts for $NO_x$ storage/reduction, Appl. Clay Sci., 29, No. 3-4, 258-266. DOI: 10.1016/j.clay.2005.02.002

Fridell E., Skoglundh M., Westerberg B., Johansson S. and Smedler G.: 1999, $NO_x$ storage in barium-containing catalysts, J. Catal. 183, No. 2, 196–209. DOI: 10.1006/jcat.1999.2415

Fung, J. and Wang, I.: 1996, The reaction mechanism of $C_6$ hydrocarbons over acid-base bifunctional catalysts, $TiO_2$-$ZrO_2$, J. Catal., 164, No. 1, 166–172. DOI: 10.1006/jcat.1996.0372

Gill, L.J., Blakeman, P.G., Twigg, M.V., Walker, A.P.: 2004, The use of $NO_x$ adsorber catalysts on diesel engines, Top. Catal., 28, No. 1-4, 157-164. DOI: 10.1023/B:TOCA.0000024345.85369.73

Hachisuka, I., Hirata, H., Ikeda, Y. and Matsumoto, S.: 2000, Deactivation mechanism of $NO_x$ storage-reduction catalyst and improvement of its performance, SAE Technical Paper 01196.

Han, P.H., Lee, Y.K., Han, S.M. and Rhee, H.K.: 2001, $NO_x$ storage and reduction catalysts for automotive lean-burn engines: Effect of parameters and storage materials on $NO_x$ conversion, Top. Catal., 16-17, No. 1-4, 165–170. DOI: 10.1023/A:1016659620699

Hendershot, R.J., Fanson, P.T., Snively, C.M. and Lauterbach, J.: 2003, High-throughput catalytic science: parallel analysis of transients in catalytic reactions, Angew. Chem. Int. Ed. 42, No. 10, 1152–1155. DOI: 10.1002/anie.200390303

Hendershot, R.J., Rogers, W.B., Snively, Ch.M., Ogunnaikea, B.A. and Lauterbach, J.: 2004, Development and optimization of $NO_x$ storage and reduction catalysts using statistically guided high-throughput experimentation, Catal. Today, 98, No. 3, 375–385. DOI: 10.1016/j.cattod.2004.08.005

Hendershot, R.J., Vijay, R., Snively, Ch.M. and Lauterbach, J.: 2007, Response surface study of the performance of lean $NO_x$ storage catalysts as a function of reaction conditions and catalyst composition, Appl. Catal. B, 70, No. 1-4, 160–171. DOI: 10.1016/j.apcatb.2005.11.020

Huang, H.Y., Long, R.Q. and Yang, R.T.: 2001a, The promoting role of noble metals on $NO_x$ storage catalyst and mechanistic study of $NO_x$ storage under lean-burn conditions, Energ. Fuel, 15, No. 1, 205–213. DOI: 10.1021/ef0001235

Huang, H.Y., Long, R.Q. and Yang, R.T.: 2001, A highly sulfur resistant Pt-Rh/$TiO_2$/$Al_2O_3$ storage catalyst for $NO_x$ reduction under lean-rich cycles, Appl. Catal. B, 33, No. 2, 127–136. DOI: 10.1016/S0926-3373(01)00176-X

Imagawa, H., Tanaka, T., Takahashi, N., Matsunaga, S., Suda, A. and Shinjoh, H.: 2007, Synthesis and characterization of $Al_2O_3$ and $ZrO_2$-$TiO_2$ nano-composite as a support for $NO_x$ storage-reduction catalyst, J. Catal., 251, No. 2, 315–320. DOI: 10.1016/j.jcat.2007.08.002

Imagawa, H., Takahashi, N., Tanaka, T., Matsunaga, S. and Shinjoh, H: 2009, Improved $NO_x$ storage-reduction catalysts using $Al_2O_3$ and $ZrO_2$-$TiO_2$ nanocomposite support for thermal stability and sulfur durability, Appl. Catal. B, 92, No. 1-2, 23–29. DOI: 10.1016/j.apcatb.2009.07.027

Ito, K., Kakino, S., Ikeue, K. and Machida, M.: 2007, NO adsorption/desorption property of $TiO_2$-$ZrO_2$ having tolerance to $SO_2$ poisoning, Appl. Catal. B, No. 74, No. 1-2, 137–143. DOI: 10.1016/j.apcatb.2007.02.008

Kabin, K.S., Muncrief, R.L. and Harold, M.P.: 2004, $NO_x$ storage and reduction on a Pt/BaO/alumina monolithic storage catalyst, Catal. Today 96, No. 1-2, 79–89. DOI: 10.1016/j.cattod.2004.05.008

Kanazawa T.: 2004, Development of hydrocarbon adsorbents, oxygen storage materials for three-way catalysts and $NO_x$ storage-reduction catalyst, Catal. Today 96, No. 3, 171–177. DOI: 10.1016/j.cattod.2004.06.119

Kantcheva, M. and Vakkasoglu, A.S.: 2004, Cobalt supported on zirconia and sulfated zirconia I.: FT-IR spectroscopic characterization of the $NO_x$ species formed upon NO adsorption and NO/$O_2$ coadsorption, J. Catal., 223, No. 2, 352–363. DOI: 10.1016/j.jcat.2004.02.007

Kobayashi, T., Yamada, T. and Kayano, K.: 1997, Study of $NO_x$ trap reaction by thermodynamic calculation, SAE Technical Paper 970745.

Kustov, A.L. and Makkee, M.: 2009, Application of $NO_x$ storage/release materials based on alkali-earth oxides supported on $Al_2O_3$ for high-temperature diesel soot oxidation, Appl. Catal. B, 88, No. 3-4, 263–271. DOI: 10.1016/j.apcatb.2008.11.013

Kwak, J.H., Kim, D.H., Szanyi, J. and Peden, C.H.F.: 2008, Excellent sulfur resistance of Pt/BaO/$CeO_2$ lean $NO_x$ trap catalysts, Appl. Catal. B, 84, No. 3-4, 545–551. DOI: 10.1016/j.apcatb.2008.05.009

Lai, S.Y., Pan, W. and Ng, C.F.: 2000, Catalytic hydrolysis of dichlorodifluoromethane (CFC-12) on unpromoted and sulfate promoted $TiO_2$-$ZrO_2$ mixed oxide catalysts, Appl. Catal. B, 24, No. 3-4, 207–217. DOI: 10.1016/S0926-3373(99)00107-1

Laurent, F., Pope, C.J., Mahzoul, H., Delfosse, L. and Gilot, P.: 2003, Modelling of $NO_x$ adsorption over $NO_x$ adsorbers, Chem. Eng. Sci., 58, No. 9, 1793–1803. DOI: 10.1016/S0009-2509(03)00014-9

Lesage, T., Saussey, J., Malo, S., Hervieu, M., Hedouin, C., Blanchard, G. and Daturi, M.: 2007, Operando FTIR study of $NO_x$ storage over a Pt/K/Mn/$Al_2O_3$-$CeO_2$ catalyst, Appl. Catal. B, 72, No. 1-2, 166–177. DOI: 10.1016/j.apcatb.2006.10.013

Li, L.D., Yu, J.J., Hao, Z.P. and Xu, Z.P.: 2007, Novel Ru-Mg-Al-O catalyst derived from hydrotalcite-like compound for NO storage/decomposition/reduction, J. Phys. Chem. C, 111, No. 28, 10552–10559. DOI: 10.1021/jp0678352

Lietti L., Forzatti P., Nova I. and Tronconi E.: 2001, $NO_x$ storage reduction over Pt-Ba/γ-$Al_2O_3$ Catalyst, J. Catal. 204, No. 1, 175–191. DOI: 10.1006/jcat.2001.3370

Liotta, L.F., Macaluso, A., Arena, G.E, Livi, M., Centi, G. and Deganello, G.: 2002, A study of the behaviour of Pt supported on $CeO_2$-$ZrO_2$/$Al_2O_3$-BaO as $NO_x$ storage-reduction catalyst for the treatment of lean burn engine emissions, Catal. Today, 75, No. 1-4, 439–449. DOI: 10.1016/S0920-5861(02)00094-9

Liu, Y., Meng, M., Li, X.G., Guo, L.H. and Zha, Y.Q.: 2008a, $NO_x$ storage behavior and sulfur-resisting performance of the third-generation NSR catalysts Pt/K/$TiO_2$-$ZrO_2$, Chem. Eng. Res. Des., 86, No. 8, 932–940. DOI: 10.1016/j.cherd.2008.02.010

Liu, Y., Meng, M., Zou, Z.Q., Li, X.G. and Zha, Y.Q.: 2008b, In situ DRIFTS investigation on the $NO_x$ storage mechanisms over Pt/K/$TiO_2$-$ZrO_2$ catalyst, Catal. Commun., 10, No. 2, 173–177. DOI: 10.1016/j.catcom.2008.08.014

Liu, G. and Gao, P.-X.: 2011, A review of $NO_x$ storage/reduction catalysts: mechanism, materials and degradation studies, Catal. Sci. Technol. 1, No. 4, 552–568. DOI: 10.1039/c1cy00007a

Luo, J.Y., Meng, M., Zha, Y.Q., Xie, Y.N., Hu, T.D., Zhang, J. and Liu, T.: 2008, A comparative study of Pt/Ba/$Al_2O_3$ and Pt/Fe-Ba/$Al_2O_3$ NSR catalysts: New insights into the interaction of Pt-Ba and the function of Fe, Appl. Catal. B, 78, No. 1-2, 38–52. DOI: 10.1016/j.apcatb.2007.08.017

Machida, M. Uto, D. Kurogi, T. and Kijima, T.: 2000, $MnO_x$-$CeO_2$ binary oxides for catalytic $NO_x$ sorption at low temperatures. Sorptive removal of $NO_x$, Chem. Mater., 12, No. 10, 3158–3164. DOI: 10.1021/cm000207r

Machida, M., Kurogi, D. and Kijima, T.: 2003, Role of hydrogen-spillover in $H_2$-NO reaction over Pd-supported $NO_x$-adsorbing material, $MnO_x$-$CeO_2$, J. Phys. Chem. B, 107, No. 1, 196–202. DOI: 10.1021/jp026321+

Matsumoto, S., Ikeda, Y., Suzuki, H., Ogai, M. and Miyoshi, N.: 2000, $NO_x$ storage-reduction catalyst for automotive exhaust with improved tolerance against sulfur poisoning, Appl. Catal. B, 25, No. 2-3, 115–124. DOI: 10.1016/S0926-3373(99)00124-1

Mahzoul, H., Brilhac, J.F. and Gilot, P.: 1999, Experimental and mechanistic study of $NO_x$ adsorption over $NO_x$ trap catalysts, Appl. Catal. B, 20, No. 1, 47–55. DOI: 10.1016/S0926-3373(98)00093-9

Milt, V.G., Querini, C.A., Miró, E.E. and Ulla, M.A.: 2003, Abatement of diesel exhaust pollutants: $NO_x$ adsorption on Co,Ba,K/$CeO_2$ catalysts, J. Catal., 220, No. 2, 424–432. DOI: 10.1016/S0021-9517(03)00285-9

Nakatsuji, T., Yasukawa, R., Tabata, K., Ueda, K. and Niwa, M.: 1999, A highly durable catalytic $NO_x$ reduction in the presence of $SO_x$ using periodic two steps, an operation in oxidizing conditions and a relatively short operation in reducing conditions, Appl. Catal. B, 21, No. 2, 121–131. DOI: 10.1016/S0926-3373(99)00015-6

Ozawa, M., Kimura, M. and Isogai, A.: 1991, Reduction reaction of lanthanum-added cerium dioxide with carbon monoxide, J. Mater. Sci., 26, No. 17, 4818–4822. DOI: 10.1007/BF00612423

Ozawa, M., Kimura, M. and Isogai, A.: 1993, The application of Ce-Zr oxide solid solution to oxygen storagepromoters in automotivecatalysts, J. Alloys Comp., 193, No. 1-2, 73–75. DOI: 10.1016/0925-8388(93)90314-D

Palomares, A.E., Uzcategui, A. and Corma, A.: 2008, $NO_x$ storage/reduction catalysts based in cobalt/copper hydrotalcites, Catal. Today, 137, No. 2-4, 261–266. DOI: 10.1016/j.cattod.2007.12.137

Park, J.-H., Cho, H., Park, S., Nam, I.-S., Yeo, G., Kil, J., Youn, Y.: 2007a, Role of cobalt on $\gamma$-$Al_2O_3$ based $NO_x$ storage catalyst, Top. Catal. 42/43, No. 1, 61-64. DOI: 10.1007/s11244-007-0152-8

Park, S.M., Park, J.W., Ha, H.-P., Han, H.-S. and Seo, G.: 2007b, Storage of $NO_2$ on potassium oxide co-loaded with barium oxide for $NO_x$ storage and reduction (NSR) catalysts, J. Mol. Catal. A, 273, No. 1-2, 64–72. DOI: 10.1016/j.molcata.2007.03.067

Park, S.J., Ahn, H.A., Heo, I.J., Nam, I.-S., Lee, J.H., Youn, Y.K. and Kim, H.J.: 2010, Hydrotalcite as a support for $NO_x$ trap catalyst, Top. Catal., 53, No. 1-2, 57–63. DOI: 10.1007/s11244-009-9435-6

Peralta, M.A., Milt, V.G., Cornaglia, L.M. and Querini, C.A.: 2006, Stability of Ba,K/$CeO_2$ catalyst during diesel soot combustion: effect of temperature, water, and sulfur dioxide, J. Catal. 242, No. 1, 18–130. DOI: 10.1016/j.jcat.2006.05.025

Qi, G. and Yang, R.T.: 2003, Performance and kinetics study for low-temperature SCR of NO with $NH_3$ over $MnO_x$-$CeO_2$ catalyst, J. Catal., 217, No. 2, 434–441. DOI: 10.1016/S0021-9517(03)00081-2

Roy, S., van Vegten, N. and Baiker, A.: 2010, Single-step flame-made Pt/$MgAl_2O_4$ - a $NO_x$ storage-reduction catalyst with unprecedented dynamic behavior and high thermal stability, J. Catal. 271, No. 1, 125–131. DOI: 10.1016/j.jcat.2010.02.017

Sakamoto, Y., Higuchi, K., Takahashi, N., Yokota, K., Doi, H. and Sugiura, M.: 1999, Effect of the addition of Fe on catalytic activities of Pt/Fe/$\gamma$-$Al_2O_3$ catalyst, Appl. Catal. B, 23, No. 2-3, 159–167. DOI: 10.1016/S0926-3373(99)00074-0

Salasc, S., Skoglundh, M. and Fridell, E.: 2002, A comparison between Pt and Pd in $NO_x$ storage catalysts, Appl. Catal. B, 36, No.2, 145–160. DOI:10.1016/S0926-3373(01)00300-9

Silletti, B.A., Adams, R.T., Sigmon, S.M., Nikolopoulos, A., Spivey, J.J. and Lamb, H.H.: 2006, A novel Pd/$MgAlO_x$ catalyst for $NO_x$ storage-reduction, Catal. Today, 114, No. 1, 64–71. DOI: 10.1016/j.cattod.2006.02.003

Strobel, R., Krumeich, F., Pratsinis, S.E. and Baiker, A.: 2006, Flame-derived Pt/Ba/$Ce_xZr_{1-x}O_2$: influence of support on thermal deterioration and behavior as $NO_x$ storage-reduction catalysts, J. Catal., 243, No. 2, 229–238. DOI: 10.1016/j.jcat.2006.07.016

Su, Y., Kabin, K.S., Harold, M.P. and Amiridis, M.D.: 2007, Reactor and in situ FTIR studies of Pt/BaO/$Al_2O_3$ and Pd/BaO/$Al_2O_3$ $NO_x$ storage and reduction (NSR) catalysts, Appl. Catal. B, 71, No. 3-4, 207–215. DOI: 10.1016/j.apcatb.2006.09.006

Takahashi, N., Shinjoh, H., Iijima, T., Suzuki, T., Yamazaki, K., Yojota, K., Suzuki, H., Miyoshi, N., Matsumoto, S., Tanizawa, T., Tanaka, T., Tateishi, S. and Kasahara, K.: 1996, The new concept 3-way catalysts for automative lean-burn engine: $NO_x$ storage and reduction catalysts, Catal. Today, 27, No. 1-2, 63–69. DOI: 10.1016/0920-5861(95)00173-5

Takeuchi, M. and Matsumoto, S.: 2004, $NO_x$ storage-reduction catalysts for gasoline engines, Top. Catal. 28, No. 1-4, 151–156. DOI: 10.1023/B:TOCA.0000024344.91688.e4

Takahashi, N., Matsunaga, S., Tanaka, T., Sobukawa, H. and Shinjoh, H.: 2007a, New approach to enhance the $NO_x$ storage performance at high temperature using basic $MgAl_2O_4$ spinel suport, Appl. Catal. B, 77, No. 1-2, 73–78. DOI: 10.1016/j.apcatb.2007.07.007

Takahashi, N., Suda, A., Hachisuka, I., Sugiura, M., Sobukawa, H. and Shinjoh, H.: 2007b, Sulfur durability of $NO_x$ storage and reduction catalyst with supports of $TiO_2$, $ZrO_2$ and $ZrO_2$-$TiO_2$ mixed oxides, Appl. Catal. B, 72, No. 1-2, 187–195. DOI: 10.1016/j.apcatb.2006.10.014

Toops, T.J., Smith, D.B., Epling, W.S., Parks, J.E. and Partridge, W.P.: 2005, Quantified $NO_x$ adsorption on Pt/K/gamma-$Al_2O_3$ and the effects of $CO_2$ and $H_2O$, Appl. Catal. B, 58, No. 3-4, 255–264. DOI: 10.1016/j.apcatb.2004.10.022

Toops, T.J., Smith, D.B. and Partridge, W.P.: 2006, $NO_x$ adsorption on $Pt/K/Al_2O_3$, Catal. Today, 114, No. 1, 112–124. DOI: 10.1016/j.cattod.2006.02.006

Toubeli, A., Efthimiadis, E.A. and Vasalos, I.A.: 2000, NO reduction by $C_3H_6$ in excess oxygen over fresh and sulfated Pt- and Rh-based catalysts, Catal. Lett., 69, No. 3-4, 157–164. DOI: 10.1023/A:1019074007397

Wang, X., Yu, Y. and He, H.: 2010, Effect of Co addition to $Pt/Ba/Al_2O_3$ system for $NO_x$ storage and reduction, Appl. Catal. B, 100, No. 1-2, 19–30. DOI: 10.1016/j.apcatb.2010.07.001

Vijay, R., Hendershot, R.J., Rivera-Jimenez, S.M., Rogers, W.B., Feist, B.J., Snively, C.M. and Lauterbach, J.: 2005, Noble metal free $NO_x$ storage catalysts using cobalt discovered via high-throughput experimentation, Catal. Commun., 6, No. 2, 167–171. DOI: 10.1016/j.catcom.2004.12.004

Vijay, R., Snively, C.M., Lauterbach, J.: 2006, Performance of Co-containing $NO_x$ storage and reduction catalysts as a function of cycling condition, J. Catal., 243, No. 2, 368-375. DOI: 10.1016/j.jcat.2006.08.005

Xiao, J., Li, X., Deng, S., Wang, F. and Wang, L.: 2008, $NO_x$ storage-reduction over combined catalyst $Mn/Ba/Al_2O_3$-$Pt/Ba/Al_2O_3$, Catal. Commun. 9, No. 5, 563–567. DOI: 10.1016/j.catcom.2006.09.020

Yamazaki, K., Suzuki, T., Takahashi, N., Yokota, K. and Sugiura, M.: 2001, Effect of the addition of transition metals to $Pt/Ba/Al_2O_3$ catalyst on the $NO_x$ storage-reduction catalysis under oxidizing conditions in the presence of $SO_2$, Appl. Catal. B, 30, No. 3-4, 459–468. DOI: 10.1016/S0926-3373(00)00263-0

Yamazaki, K., Takahashi, N., Shinjoh, H. and Sugiura, M.: 2004, The performance of $NO_x$ storage-reduction catalyst containing Fe-compound after thermal aging, Appl. Catal. B, 53, No. 1, 1–12. DOI: 10.1016/j.apcatb.2004.04.010

Yamamoto, K., Kikuchi, R., Takeguchi, T. and Eguchi, K.: 2006, Development of NO sorbents tolerant to sulfur oxides, J. Catal., 238, No. 2, 449–457. DOI: 10.1016/j.jcat.2006.01.006

Yu, J.J., Jiang, Z., Zhu, L., Hao, Z.P. and Xu, Z.P.: 2006, Adsorption/desorption studies of $NO_x$ on well-mixed oxides derived from Co-Mg/Al hydrotalcite-like compounds, J. Phys. Chem. B, 110, No. 9, 4291–4300. DOI: 10.1021/jp056473f

Yu, J.J., Tao, Y.X., Liu, Ch.Ch., Hao, Z.P. and Xu, Z.P.: 2007a, Novel NO trapping catalysts derived from Co-Mg/X-Al (X = Fe, Mn, Zr, La) hydrotalcite-like compounds, Environ. Sci. Technol., 41, No. 4, 1399–1404. DOI: 10.1021/es061538t

Yu, J.J., Wang, X.P., Li, L.D., Hao, Z.P. and Xu, Z.P.: 2007b, Novel multi-functional mixed-oxide catalysts for effective $NO_x$ capture, decomposition, and reduction, Adv. Funct. Mater., 17, No. 17, 3598–3606. DOI: 10.1002/adfm.200700334

Yu, J.J., Wang, X.P., Tao, Y.X. and Hao, Z.P.: 2007c, Effective $NO_x$ decomposition and storage/reduction over mixed oxides derived from layered double hydroxides, Ind. Eng. Chem. Res., 46, No. 17, 5794–5797. DOI: 10.1021/ie0705958

Yu, J.J., Vheng, J., Ma, Ch.Y., Wang, H.L., Li, L.D., Hao, Z.P. and Xu, Z.P.: 2009, $NO_x$ decomposition, storage and reduction over novel mixed oxide catalysts derived from hydrotalcite-like compounds, J. Coll. Int. Sci., 333, No. 2, 423–430. DOI: 10.1016/j.jcis.2009.02.022

Zou, Z.Q., Meng, M., Tsubaki, N., He, J.J., Wang, G., Li, X.G. and Zhou, X.Y.: 2009, Influence of Co or Ce addition on the $NO_x$ storage and sulfur-resistance performance of the lean-burn $NO_x$ trap catalyst $Pt/K/TiO_2$-$ZrO_2$, J. Hazard. Mater. 170, No. 1, 118–126. DOI: 10.1016/j.jhazmat.2009.04.125