



REVIEW

**A SHORT REVIEW ABOUT NO_x STORAGE/REDUCTION CATALYSTS
BASED ON METAL OXIDES AND HYDROTALCITE-TYPE ANIONIC CLAYS****Magdalena JABŁOŃSKA¹⁾, Antonio Eduardo PALOMARES GIMENO²⁾*,
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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, NO₂), 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.%)/Al₂O₃, 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 NO₂ on the Pt active sites, and NO₂ is adsorbed on BaO as nitrate, (ii) under rich conditions, nitrates decompose and NO₂ formed is reduced into N₂ with HC, CO and H₂ present in the exhaust gases (Palomares et al., 2008). The possible mechanism of NO_x storage/reduction in the presence of typical Pt/Ba/Al₂O₃ catalysts is presented in Figure 1.

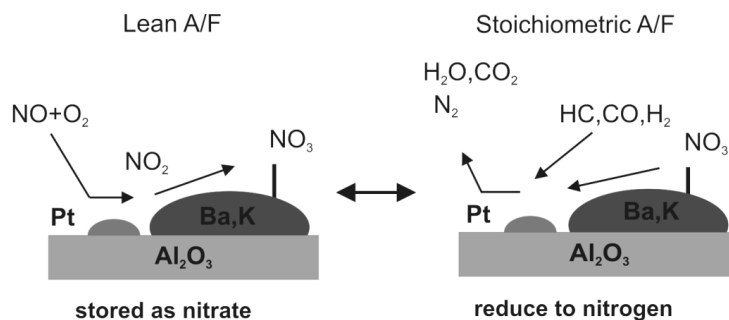


Fig. 1 The mechanism of NO storage in exhaust gas from lean mixture combustion and their reduction in exhaust gas from rich mixture combustion; symbols: Pt - platinum crystallite, Ba, K - NO_x storing component (Kanazawa, 2004).

The Pt/Ba/Al₂O₃ 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 SO₂ in the exhaust, even at trace amounts, because of the irreversible adsorption of SO₂ 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 SO₂-tolerant NSR catalysts with comparable or better performance for NSR.

2.1. METAL OXIDE SUPPORTS

In the early literature the Pt/Ba/Al₂O₃ 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

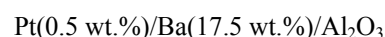
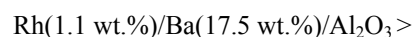
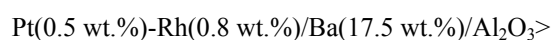
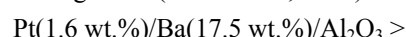
adsorption achieved at 300 °C over Pt (1.0 wt.%) / Ba (10.0 wt.%) / Al₂O₃ was higher (0.700 mmol(NO)/g) compared to the result obtained with Pt (1.0 wt.%) / Ba(20.0 wt.%) / Al₂O₃ (0.581 mmol(NO)/g). However, the amount of NO_x stored on the catalysts in terms of available surface area was much higher in case of the smallest amount of Ba (Lietti et al., 2001). Further research was carried out on the Pt/Ba/Al₂O₃ 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.%) / Al₂O₃ catalysts exhibited the highest NO_x storage capacity (3.500 mol(NO)/g). Moreover, it was shown that the Pt/Ba/Al₂O₃ 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/Al₂O₃ 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.%) / Al₂O₃ 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.%) / Al₂O₃, by using C₂H₄ 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.%) / Al₂O₃ washcoat monolith catalysts for NO_x storage and reduction was analyzed (Kabin et al., 2004). Authors determined the reductant (C₃H₆) 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 % O₂ 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/Al₂O₃ 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.%) / Al₂O₃ 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.%)/Al₂O₃, Ba (20.0 wt.%)/Al₂O₃, Pt (2.0 wt.%)-Rh (1.0 wt.%)/Al₂O₃ and Pt (2.0 wt.%)-Rh (1.0 wt.%(20.0 wt.%)/Ba/Al₂O₃ 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 NO₂ storage capacity were observed. In similar line, the NO_x storage/reduction activity between Pt (3.0 wt.%)/Ba (20.0 wt.%)/Al₂O₃ and Pd (3.0 wt.%)/Ba (20.0 wt.%)/Al₂O₃ were compared using lean-burn exhaust containing NO, O₂, C₂H₆ and N₂ (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/Al₂O₃ catalyst was found to exhibit greater low temperature of the NO_x storage capacity than Pt/Ba/Al₂O₃ (0.031 and 0.033 mole NO_x per mole Ba, respectively). Authors explained the differences between Pt- and Pd/BaO/Al₂O₃ 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.%)/Al₂O₃ 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.%)/Al₂O₃.

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/Al₂O₃ 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/Al₂O₃ catalysts was lower than that the other two metal-based NSR catalysts. The low NSR activity of Rh/Ba/Al₂O₃ 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 % H₂ + 4.5 % CO

reductant mixture at 350 °C) was found to be presented in the following order (Breen et al., 2008):



Further studies confirmed lower NO_x trapping capacity and NO oxidation activity for Pt-Rh/Ba/Al₂O₃ compared to the Pt/Ba/Al₂O₃ 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.%)/Al₂O₃ was 0.116 related to 0.061 achieved for Pt (2.0 wt.%)-Rh (1.0 wt.%)/Ba (13.0 wt.%)/Al₂O₃ catalyst. Nevertheless, NO_x reduction activity over the Pt-Rh/Ba/Al₂O₃ catalysts was better than that for the Pt/Ba/Al₂O₃ 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/Al₂O₃ catalysts.

2.1.1. TRANSITION METAL – DOPED CATALYSTS

The effect of the transition metals addition (e.g. Co, Ni, Cu, Fe) to the Pt/Al₂O₃ or Pt/Ba/Al₂O₃ 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.%)/Al₂O₃ catalysts decreased its activity, e.g. at 300 °C the NO_x mean conversion for Pt-Cu/Ba/Al₂O₃ was about 60 % compared to around 95 % achieved for the Pt/Ba/Al₂O₃ 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.%)/Al₂O₃ or Pt(1.67 wt.%)/Al₂O₃, 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.%)/Al₂O₃ or Pt (1.67 wt.%)/Ba(34.3 wt.%)/Al₂O₃ 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/Al₂O₃ catalyst and nearly equal or even slightly higher than that of the fresh Pt/Al₂O₃ catalysts— at every tested temperature, respectively. In addition, it was reported that introduction of Fe (1.1 wt.%) to the Pt(3.7 wt.%)/Al₂O₃ catalysts had not significant effect in the reactivity of Pt on the Pt/Fe/Al₂O₃ catalysts after being heated in flow of 7.5 % O₂/N₂ (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.%) / Al₂O₃ and Pt

(1.5 wt.%)/Fe(11.0 wt.%)/Ba(28.0 wt.%)/Al₂O₃ 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/Al₂O₃ structure was performed (Luo et al., 2008). It was observed, that after introduction of Fe (7.6 wt.%) to Ba (15.0 wt.%)/Al₂O₃ 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 Fe₂O₃ had a positive effect on the NO_x storage. The fresh Pt (1.5 wt.%) promoted catalysts displayed similar storage profiles comparing to Ba/Al₂O₃ and Fe-Ba/Al₂O₃. After reduction pretreatment (under pure hydrogen at 500 °C for 1 h) of the Pt-Fe/Ba/Al₂O₃ 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.%) / Al₂O₃ or Ba (15.0 wt.%)/Al₂O₃ 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.%)/Al₂O₃ catalysts was found to store NO_x (0.030 mmol) as efficiently as Pt (1.0 wt.%) / Ba (15.0 wt.%) / Al₂O₃. 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 (Co₃O₄) (Park et al., 2007a). It was proposed that Co₃O₄ 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/Al₂O₃ system was also reported (Vijay et al., 2005). The Pt (1.0 wt.%) /Co (5.0 wt.%)/Ba (20.0 wt.%)/Al₂O₃ 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.%) / Al₂O₃ and Rh (1.0 wt.%) / Ba (15.0 wt.%)/Al₂O₃ 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/Al₂O₃ and Pt/Ba/Al₂O₃ catalysts by 50 and 100 % under long-cycling conditions, respectively. The performance of the Co-Pt/Ba/Al₂O₃ 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/Al₂O₃, Sr/Al₂O₃, Ca/Al₂O₃ or Mg/Al₂O₃ 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/Al₂O₃ (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.%)/Al₂O₃ 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.%)/Al₂O₃ catalyst exhibited an intermediated activity between those of the Pt/Ba/Al₂O₃ sample at temperatures 200-300 °C, although associated with a complete absence of activity at 500 °C. The Pt (1.0 wt.%) / Ba (8.5 wt.%) -Mg (1.5 wt.%) / Al₂O₃ 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/Al₂O₃ 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 SO₂.

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.)/Al₂O₃(0.052 mmol/g) <

Pd(1.0 wt.)/Ca(5.0 wt.)/Al₂O₃ (0.097 mmol/g) <

Pt(1.0 wt.)/Ca(5.0 wt.)/Al₂O₃ (0.180 mmol/g) <

Rh(1.0 wt.)/Ca(5.0 wt.)/Al₂O₃ (0.280 mmol/g).

The authors claimed that the addition of Rh provided better NO_x storage ability for a series of the Ca/Al₂O₃ catalysts, compared to Pt, due to more effective NO₂ formation. This statement, however, was contradicted by several studies on the Al₂O₃-supported Pt and/or Rh catalysts. For example, the same activity for NO oxidation over Rh/Al₂O₃ and Pt/Al₂O₃ was reported (Kobayashi et al., 1997). It was shown that in the presence of the Rh (2.0 wt.)/Al₂O₃ catalyst not more than 30 % of inlet NO is oxidized to NO₂ in the presence of C₃H₆ at 400 °C. The Pt-counterpart catalysts in all cases were reported to provide higher amounts of NO₂ 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 K₂O 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/Al₂O₃ (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.)/Al₂O₃ 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.%) / Al₂O₃ 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)/MgAl₂O₄ catalysts, in which the spinel (MgAl₂O₄) 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/MgAl₂O₄ catalysts were apparently higher than those obtained for the K/Pt/Al₂O₃ catalysts. For example, the relative NO_x storage capacity measured for the fresh Pt (0.07 g)-K (2.0 g)/MgAl₂O₄ catalyst was about 4 (a.u) compared to about 2 (a.u) achieved for the fresh Pt (0.07 g)-K

(2.0 g)/Al₂O₃ sample at 600 °C. In similar line, the Ba- or K-free Pt(1.0 wt.)/MgAl₂O₄ catalyst obtained by single-step flame made also was studied (Roy et al., 2010). The catalysts containing of nano-sized Pt dispersed on MgAl₂O₄ 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/MgAl₂O₄ at 350 °C was about 87 % compared to 70 % for the reference Pt (1.0 wt.%) / Ba (20.0 wt.)/Al₂O₃ catalyst. Moreover, the Pt/MgAl₂O₄ 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/Al₂O₃ 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 SO₂ (Xiao et al., 2008; Yamazaki et al., 2001; Hendershot et al., 2004) were proposed. Studies focused mainly on the modification of the support (Al₂O₃) were reported to improve the NSR activity.

The benefit of the Ce-promoted catalysts is sulfur resistance since it is known that SO₂ 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 CeO₂ and Al₂O₃ as the supports was compared (Kwak et al., 2008). The Pt (2.0 wt.%) / Ba (10.0 wt.%) / CeO₂ sample exhibited slightly higher NO_x uptake compared to Pt (2.0 wt.)/Ba (20.0 wt.)/Al₂O₃, and the additionally the CeO₂-based catalysts showed higher sulfur tolerance than the Al₂O₃-based one. The NO_x uptake at 250 °C, obtained for the CeO₂-based catalysts was about 60 % which was significantly higher than 49 % measured for the Al₂O₃-based catalyst. NO_x uptake of the SO₂-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.)/CeO₂ exhibited inferior NO_x storage performance, particularly the reduction/regeneration activity compared to the Al₂O₃ supported catalysts (Casapu et al., 2008). Authors proposed that the incomplete reduction of stored NO_x species by Pt/Ba/CeO₂ was caused by faster and more profound re-oxidation of Pt particles during the lean period.

The Ba(Co,K)/CeO₂ system was studied as potential candidate for the NO_x abatement from diesel exhaust (Milt et al., 2003). The NO₂ storage capacity of the Ba (16.0 wt.%)/CeO₂ sample was 63.1 %, while the NO₂ storage capacity of the K (7.0 wt.%) / Ba (16.0 wt.%) / CeO₂ sample was 44.7 %. For the Co (12.0 wt.%) - K (7.0 wt.%) / Ba (16.0 wt.%) / CeO₂ sample, the solid storage capacity was very small in the presence of NO or NO + O₂. However, the NO₂ storage capacity of this sample at 300 °C (27.1 %) was comparable to that of Pt/Ba/Al₂O₃ (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.%) / Al₂O₃ - CeO₂ (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/Al₂O₃ catalyst (Lietti et al., 2001). However, NO_x storage determined for full catalyst saturation for Pt/Ba/Al₂O₃ was 0.324 mmol/g at 400 °C compared to 0.675 mmol/g achieved for the Pt-Mn-K/Al₂O₃-CeO₂ catalysts. In similar line, the Pt (0.83 wt.%) / Ba (19.1 wt.%) / Al₂O₃ - CeO₂ (20.4 wt.%) and the Pt (0.83 wt.%) / Ba (19.1 wt.%) / Al₂O₃ - CeO₂ (20.4 wt.%) - Fe₂O₃ (3.3-13.2 wt.%) catalysts were studied (Yamazaki et al., 2004). The fresh Pt/Ba/Al₂O₃-CeO₂-Fe₂O₃ (6.6 wt.%) catalyst showed the same NSR activity as fresh Pt/Ba/Al₂O₃-CeO₂ when either C₃H₆ 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 C₃H₆ was used as a reducing agent. After thermal aging at 850 °C the NO_x conversion for both the catalysts dropped to about 40 %.

CeO₂, ZrO₂ (Clacens et al., 2004) or CeO₂-ZrO₂ (Strobel et al., 2006) were tested as an alternative supports of the NSR catalysts. The CeO₂-ZrO₂ solid solution with 20 mole % of Zr was developed to improve the thermal stability of CeO₂ (Ozawa et al., 1991; Ozawa et al., 1993). In further studies, a series of the Pt/Ba/Ce_xZr_{1-x}O₂ (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 % H₂/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 prerduced Pt was active for NO_x reduction, resulting in NO_x conversion of 33.6 %. The H₂-pretreatment increased also the efficiency of the NO_x reduction for Pt deposited on ZrO₂, 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 (Al₂O₃, SiO₂, Al₂O₃-(5.5 wt.%) SiO₂, Ce_{0.7}Zr_{0.3}O₂) 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 / Al₂O₃-(5.5 wt.%) SiO₂ 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}O₂ 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.%) / Al₂O₃ samples presented high sulfur sensitivity, with almost 70 % of the NO_x storage capacity loss after catalyst sulfation.

Also TiO₂ was studied as NSR catalysts. TiO₂ is an interesting material due to its high tolerance against sulfur poisoning (Hachisuka et al., 2000; Huang et al., 2001b). Substitution BaO for TiO₂ 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.%) / TiO₂ (10.0-30.0 wt.%) / Al₂O₃ catalysts was more suitable in the presence of SO₂ due to its higher tolerance for this poison. In the presence of SO₂ and H₂O, the NO_x conversion dropped from 94 to 90 % over the Pt-Rh/TiO₂ (20.0 wt.%) / Al₂O₃ catalysts at 250 °C. Authors explained these results by lower decomposition temperature of sulfates on the TiO₂ surface (Huang et al., 2001b).

TiO₂ was used as support for the preparation of a series of Pt (1.0 wt.%) / M_xO_y (10.0 wt. %) / TiO₂ 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/TiO₂ under both SO₂-free or SO₂-containing atmospheres. The effect of the additives on the NO sorption capacity was in the following order:



The NO sorption capacity was significantly deteriorated in SO₂-containing atmosphere for all the catalysts except for Pt/TiO₂ and Pt/Li₂O/TiO₂. Total NO_x storage capacity calculated by assuming NO sorbed as nitrate over Pt-Li₂O/TiO₂ was 6.690 mmol/g at 300 °C.

Another approach studied in the literature was application of ZrO₂-TiO₂ mixture as support of the catalysts (Fung and Wang, 1996; Lai et al., 2000). The optimal TiO₂/ZrO₂ ratio was found to be 2/3 (Takahashi et al., 2007b) and the optimum calcination temperature of the TiO₂-ZrO₂ 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 TiO₂-ZrO₂ can prevent SO₂ adsorption and promote SO₂ desorption. Thus, the lean-burn NO_x trap catalysts based on such oxide system show much better sulfur-resistance than the Pt/Ba/Al₂O₃ catalysts. The effect of SO₂ on the adsorption and desorption properties of NO over TiO₂-ZrO₂ was studied by Ito et al. (Ito et al., 2007), who showed that a maximum adsorptive NO uptake of (n)TiO₂-(1-n)ZrO₂ 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 SO₂. TiO₂-ZrO₂ exhibited stable temperature-swing NO adsorption/desorption cycles in a stream of 0.16 % NO, 10 % O₂, 100 ppm SO₂ and He balance. By contrast, Al₂O₃ exhibited a significant deterioration since sulfate species block the base sites from NO_x adsorption. The tolerance of TiO₂-ZrO₂ to SO₂ 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/TiO₂-ZrO₂ 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.%) / TiO₂-ZrO₂ 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/(TiO₂-ZrO₂) 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/(TiO₂-ZrO₂) catalyst). After sulfation and regeneration, the promoted catalysts showed more or less decreased the NO_x storage capacity efficiency comparing to Pt/K/TiO₂-ZrO₂ 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 Al₂O₃, ZrO₂ and TiO₂ were evaluated as a novel support for the NSR catalysts. It was found that the mixture of TiO₂ and γ-Al₂O₃ 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 Al₂O₃ and ZrO₂-TiO₂ (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-ZrO₂ 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-CeO₂ 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.%) - CeO₂ (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.%) - CeO₂ (50.0 wt.%) (Costas and Efstathiou, 2007) or CeO₂-ZrO₂(20.0 wt.%) / Al₂O₃ (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.%) / Al₂O₃ 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 H₂O and CO₂ 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.

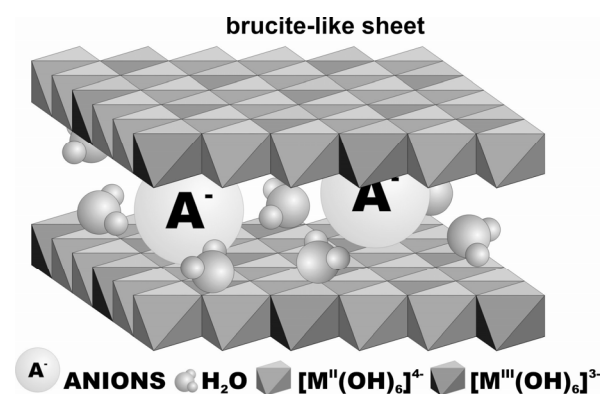


Fig. 2 Schematic representation of hydrotalcite.

The most often reported NSR catalysts derived from hydrotalcites 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.)/Al₂O₃ 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 Pt (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.)/Al₂O₃ catalysts. Moreover, the hydrotalcite-based Pt-Cu catalysts showed higher resistance for SO₂ deactivation than the Pt/Ba/Al₂O₃ 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 CH₃COOK and KNO₃ 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 CH₃COOK and KNO₃ 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 NO₂, indicating the occurrence of NO oxidation in some

way. It was noted that about 15 and 25 % NO_x was directly decomposed to N₂ as well as N₂O over these two catalysts, respectively.

In the further studies, an improvement of NSR catalysts by substitution of M^{II} (Mg²⁺) or M^{III} (Al³⁺) for other cations was reported (Centi et al., 2003; Fornasari et al., 2002; Yu et al., 2007a). Substitution of 50 % Al³⁺ in the Co/Mg/Al (25:5:10) hydrotalcite structure with Fe³⁺, Mn³⁺, Zr⁴⁺, La³⁺ and testing of such catalysts in NO_x NSR was reported (Yu et al., 2007a). The obtained results showed that La³⁺ enhanced both the storage and reduction of NO_x efficiency. In this system La₂O₃ was proposed to link the redox/storage region and lower the activation energies (Yu et al., 2009). To increase the NSR activity, instead of Mg²⁺ cations Ca²⁺ 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 N₂ and O₂ 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 Ca²⁺ cations with more basic Ba²⁺ or Sn²⁺. 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 O₂-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 H₂O and SO₂. 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 SO₂ and H₂O. 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 SO₂ (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.

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