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## **An overview of the production and use of ammonia in NSR + SCR coupled system for NO<sub>x</sub> reduction from lean exhaust gas.**

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### **Abstract**

This paper gives a critical overview of the recent advances in NO<sub>x</sub> abatement in excess of oxygen based on the combination of the NO<sub>x</sub> storage-reduction (NSR) and Selective Catalytic Reduction (SCR) processes. Ammonia may be produced during the regeneration step of NSR catalyst, by the direct reaction (NO<sub>x</sub> + H<sub>2</sub>) or/and the isocyanate route. Recent literature highlights that the ammonia production rate is higher than the ammonia reaction rate with the remaining NO<sub>x</sub> in order to form N<sub>2</sub>. In order to optimize the use of the *in situ* produced ammonia, a catalyst dedicated to the NO<sub>x</sub>-SCR by NH<sub>3</sub> can be added. Zeolites are the main studied materials for this application. Catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub> relates a complex mechanism, in which the nuclearity of the active sites is still an open question. Over zeolites, the NO to NO<sub>2</sub> oxidation step is reported as the rate-determining step of the SCR reaction, even if the first step of the reaction is ammonia adsorption on zeolite Brønsted acid sites. Thus, the addition of a NH<sub>3</sub>-SCR material to the NSR catalyst is a possible way to increase the global NO<sub>x</sub> abatement and maximize the N<sub>2</sub> selectivity, together with the prevention of the ammonia slip.

Keywords: NO<sub>x</sub>; NSR; SCR; ammonia; NH<sub>3</sub>.

## 1. Introduction

In order to reduce CO<sub>2</sub> emissions, direct-injection lean-burn engines are attractive for car manufacturers due to their lower fuel consumption. However, these engines operate with a large air excess, which makes very difficult the NO<sub>x</sub> abatement in the post combustion catalytic converters. Two catalytic solutions are envisaged to be implemented on those types of cars: (i) the NO<sub>x</sub> Selective Catalytic Reduction by NH<sub>3</sub> (NH<sub>3</sub>-SCR) or (ii) the NO<sub>x</sub>-trap system (also called NO<sub>x</sub>-Storage Reduction or NSR system). Today in Europe, the NH<sub>3</sub>-SCR technology should be implemented on heavier cars and trucks while the NSR system has been widely studied as a promising technology especially for lighter passenger cars.

The typical NO<sub>x</sub>-trap catalyst contains a noble metal (Pt) allowing the NO oxidation into NO<sub>2</sub>, a basic phase (Ba oxide/carbonate) for trapping NO<sub>2</sub> as nitrite/nitrate intermediates, these two active phases being supported on a modified alumina support. The catalytic material operates in fast lean/rich transients. NO<sub>x</sub> are firstly trapped during a lean phase of about 1 minute, while the "saturated" trap is regenerated during the rich phase of only a few seconds. The gases flowing over the catalyst during the lean phase are constituted by the standard exhaust issued from the engine. The rich phase is however generated by injecting a large pulse of fuel, immediately transformed into HC, CO and H<sub>2</sub> on a pre-catalyst (generally the Diesel Oxidation Catalyst located before the NSR system). This pulse of fuel provokes an exotherm helping the nitrate to desorb from the NSR catalyst while residual reducers (HC, CO and H<sub>2</sub>) reduce the desorbed NO<sub>x</sub> into nitrogen. These steps are describing the ideal operating mode of the NSR system. Nevertheless, other undesirable compounds can be emitted during the regeneration, especially ammonia [1,2].

In order to increase the global NO<sub>x</sub> abatement and the N<sub>2</sub> selectivity, adding a NH<sub>3</sub>-SCR catalyst to the NSR catalyst is a simple and efficient way. Ammonia produced during the short periods in rich media can be stored on the SCR catalyst, and it can further react with

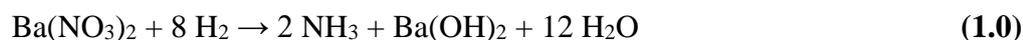
NO<sub>x</sub> passing through the NO<sub>x</sub>-trap during the next lean period. This work reports recent results about the production and use of ammonia in NSR +SCR coupled system for NO<sub>x</sub> reduction.

## 2. NH<sub>3</sub> emission from NSR catalysts

The NO<sub>x</sub> storage reduction (NSR or Lean NO<sub>x</sub> Trap –LNT-) process is largely studied since the beginning of the 1990s [3,4,5]. Alumina supported platinum based catalysts are the most investigated systems and barium oxide is usually added as NO<sub>x</sub> storage phase. It works mainly in lean condition. NO<sub>x</sub> are then oxidized on precious metals and stored on basic compounds, mainly in the form of nitrates. Periodically, the catalyst is submitted to rich condition for a few seconds, and the nitrates formed during the lean step are reduced into N<sub>2</sub> on the precious metals [6,7]. The nature of the reducers in the rich mixture directly impacts the NO<sub>x</sub> conversion and the selectivity of the NSR reaction. On usual NSR model catalysts, namely Pt/(BaO)/Al<sub>2</sub>O<sub>3</sub>, hydrogen is reported to be more efficient as reducing agent than CO [8,9]. This higher efficiency of H<sub>2</sub> is clearly evidenced by Szailer *et al.* [8] at very low temperature (150°C), and in the 150-350°C temperature range by Nova *et al.* [9]. The following section focuses on the ammonia formation and emission over NSR catalysts.

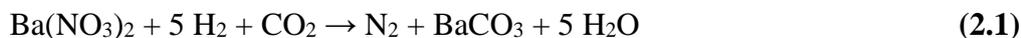
### 2.1 Ammonia formation

Ammonia can be formed by the direct reaction of stored NO<sub>x</sub> with hydrogen (Eq. (1.0)) [10,11]. This route is likewise reported in Ref. [12] over Pt-Ba/Al<sub>2</sub>O<sub>3</sub> material, when H<sub>2</sub> is used as the reducer. Artioli *et al.* [13] observed that, depending on the gas feed composition, ammonia is emitted together with CO<sub>2</sub> consumption, as reported in Eq. 1.1.

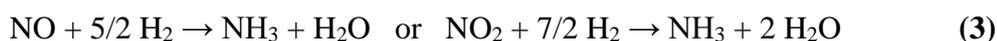


Castoldi *et al.* mentioned that ammonia emission is observed when barium loading ranges

from 16 to 30 wt.% [12]. At lower barium loading (*i.e.* 5-16 wt.%), authors have reported that the reduction of stored NO<sub>x</sub> is initially fully selective into nitrogen, according to the Eqs. (2).



The catalyst temperature is also an important parameter, impacting the NO<sub>x</sub> adsorption during the lean periods and reduction rate versus the desorption rate during the lean periods. In addition, exotherms are detected during the rich pulses, indicating that H<sub>2</sub> also reacts with remaining oxygen (from gas phase and/or catalyst), leading to an additional release of stored NO<sub>x</sub>. Then, when the regeneration of the catalyst is carried out in the presence of NO, and reaction (3) may also occur [14]:

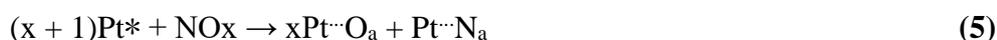


Ammonia is however observed after N<sub>2</sub> formation, when hydrogen begins to be emitted. This point is discussed below (section 2.2).

The direct ammonia formation mechanism (Eq. 1 and 3), when only H<sub>2</sub> is used as reducer, was studied in Ref. [8]. Authors proposed the hydrogen activation on the platinum surface, which first reacts with the adsorbed oxygen species (O<sub>a</sub>, Eq. 4), remaining on the Pt surface from the reduction of NO<sub>2</sub>. In Eq. 4, Pt\* denotes reduced Pt sites.



The so produced H<sub>2</sub>O destabilizes the adsorbed nitrates. Consequently, surface nitrates present over alumina are suggested to be decomposed on the Pt free surface. The dissociation of NO<sub>x</sub> species on the Pt clusters can be followed by the recombination of N<sub>a</sub> atoms to form N<sub>2</sub> (Eq. 5 and 6), or by the reaction of these N<sub>a</sub> atoms with H<sub>2</sub> to form NH<sub>x</sub> and, ultimately, NH<sub>3</sub>.



In this process, the primary role of H<sub>2</sub> is to keep the platinum surface clean and reduced for

the NO<sub>x</sub> dissociative adsorption. Indeed, the reaction of H<sub>2</sub> with O<sub>a</sub> leads to the production of H<sub>2</sub>O and free Pt<sup>0</sup> surface site (Eq. 4). It is suggested that the H<sub>2</sub> dissociative adsorption, leading to H<sub>a</sub> species, promotes the NO dissociation reaction on Pt surface [15]. Structure and temperature are also key parameters for the NH<sub>3</sub> emission. Indeed, modeling the effect of platinum dispersion of a model Pt/BaO/Al<sub>2</sub>O<sub>3</sub> sample, allowed Bhatia *et al.* [16] to propose that highest amount of NH<sub>3</sub> is produced over low dispersed catalyst (3.2% platinum dispersion) at high temperature (T ≥ 300°C). Effect of temperature in NH<sub>3</sub> formation is important since it was also observed that ammonia formation is enhanced at low temperature (T ≤ 200°C) but rather with high dispersed catalyst (50% dispersion) [16]. The effect of noble metal dispersion on ammonia production is then explained by the varying average distance – or proximity – between the stored NO<sub>x</sub> and the platinum sites. Proximity between storage sites and reaction sites affects the stored NO<sub>x</sub> transport process [17].

Ammonia can also be formed via the isocyanate route, when CO is used as the main reducer [8]. At low temperature (T < 150°C), the first reaction is the removal of adsorbed oxygen atoms over the Pt particles (Pt··O<sub>a</sub>), leading to CO<sub>2</sub> production (Eq. 7).



The obtained free Pt sites become available for the CO adsorption step as for the NO<sub>x</sub> dissociative adsorption. Then, adsorbed species can react together to form NCO species (Eq. 8).



-NCO species generated on the Pt particles spill over to the oxide components of the catalyst. Therefore, -NCO and CO<sub>2</sub> formation occur at the expense of adsorbed nitrate species, while N<sub>2</sub> is not produced. At higher temperatures (T > 300°C), these NCO species can readily react with the stored NO<sub>x</sub>. This reaction route eventually leads to the consumption of both nitrate and NCO adsorbed species (Eq. 9).



It is reported that N<sub>2</sub> formation is significantly enhanced by adding water to the NCO-covered catalysts [18]. Adding water then open up a new reaction route for the –NCO reactivity, namely the hydrolysis of NCO species to NH<sub>3</sub> and CO<sub>2</sub> (Eq. 10 and 11).

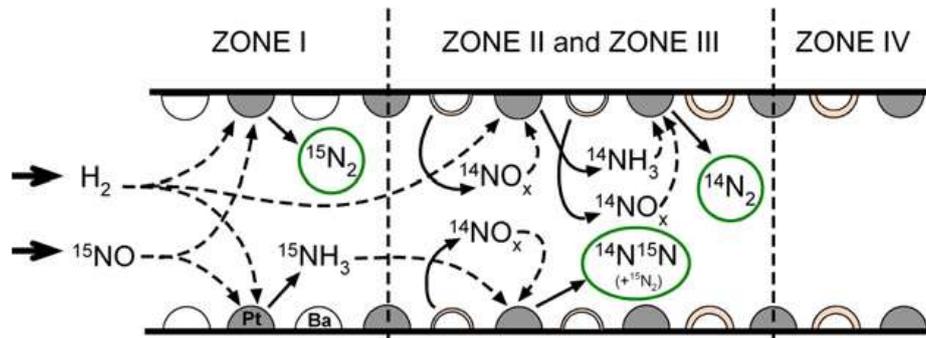


The presence of H<sub>2</sub>O and CO<sub>2</sub> in the gas mixture directly impacts ammonia formation mechanism. According to Eq. 12, the Water Gas Shift (WGS) and the reverse reaction (Reverse WGS, RWGS) can also occur, leading to the presence of both CO and H<sub>2</sub> in gas phase, even if the initial reducer in the rich mixture is H<sub>2</sub> or CO alone.



It is also demonstrated the presence of water or carbon dioxide in the gas mixture has a negative effect on the storage step of the NSR process [19,20]. However, these molecules have different impacts on the NO<sub>x</sub> abatement efficiency. Due to their involvement in the RWGS reaction, the absence of water in the gas mixture leads to a drop of the NO<sub>x</sub> removal. In opposition, the presence of CO<sub>2</sub> leads to a decreases in NO<sub>x</sub> conversion [20]. Hydrocarbons (such as propene) are also possible reducers leading to isocyanates via oximes intermediates [21]. Isocyanates lead to amines (or amides) that are very good reducers of NO<sub>x</sub> [21,22].

To conclude, ammonia can be formed either by hydrolysis of isocyanates or by direct reaction of stored NO<sub>x</sub> with H<sub>2</sub>, in the absence of NO during the regeneration [23]. Hydrogen is reported as a more efficient reducer than CO, leading to a higher emission of ammonia [8,9]. When the regeneration of the catalyst is carried out in the presence of NO, it is postulated that the incoming NO reacts with hydrogen to form NH<sub>3</sub> in the reactor zone where the trap has been already regenerated, as illustrated in scheme 1 and discussed above [14].



**Scheme 1.**

Schematic view of the proposed regeneration mechanism of the Lean NO<sub>x</sub> Trap (LNT) with hydrogen. Storage was achieved with <sup>14</sup>NO and regeneration in the presence of <sup>15</sup>NO [14].

## 2.2 Ammonia reactivity

As presented above, two primary competing routes are proposed to produce N<sub>2</sub> when H<sub>2</sub> is the reducer: (i) the direct route, from the reduction of stored NO<sub>x</sub> by H<sub>2</sub> (Eq. 1), (ii) the sequential route (Eq. 13-14) through NH<sub>3</sub> intermediate formation [24,25]:



This two-steps mechanism was evidenced in Refs. [26] and [20] over a model Pt-Ba/Al<sub>2</sub>O<sub>3</sub> catalyst. When the amount of introduced hydrogen is too low to reduce all the stored NO<sub>x</sub>, incomplete regeneration of the catalyst is observed. Such an incomplete regeneration obviously results in a decrease of the storage capacity for the subsequent lean periods. Beside, the reaction of the stored NO<sub>x</sub> with hydrogen results in the formation of negligible amount of N<sub>2</sub>O and NH<sub>3</sub>, nitrogen being the only product detected at the reactor exit. From other works [1,9], no ammonia emission over Pt-Ba/Al<sub>2</sub>O<sub>3</sub> is observed as long as hydrogen is fully consumed. It is especially true for temperature higher than 300°C. In fact, at 400°C (Fig. 1), it is reported that the NO<sub>x</sub> reduction selectivity strongly depends on the hydrogen conversion during the rich pulses [1]. The increase in H<sub>2</sub> concentration in the rich period leads to dramatically change in the N<sub>2</sub>/NH<sub>3</sub> distribution at the reactor outlet.

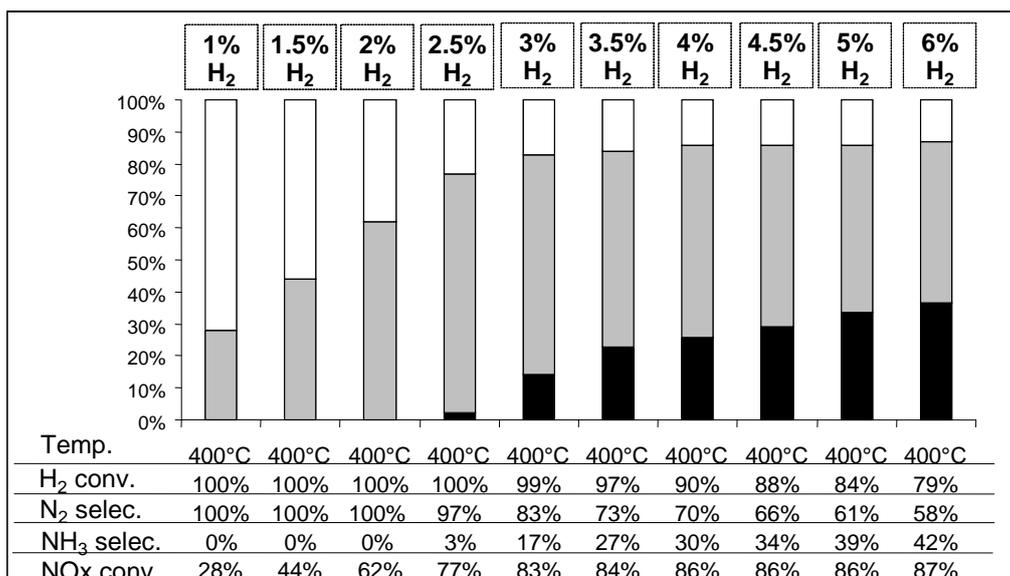


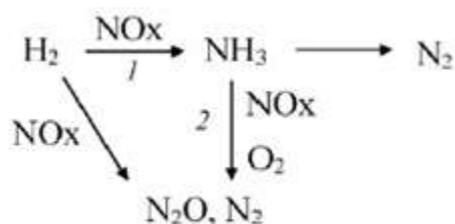
Fig. 1. Pt/Ba/Al<sub>2</sub>O<sub>3</sub> catalyst : NO<sub>x</sub> conversion at 400°C under cycling lean (60s, 500ppm NO, 10% O<sub>2</sub>, 10% H<sub>2</sub>O, 10% CO<sub>2</sub>) / rich (3s, H<sub>2</sub>, 10% H<sub>2</sub>O, 10% CO<sub>2</sub>) condition. NO<sub>x</sub> conversion (%) into N<sub>2</sub> (■) and into NH<sub>3</sub> (■) and related data. Influence of H<sub>2</sub> concentration in the rich pulses (1–6%) [1].

An overview of literature data for ammonia emission and hydrogen consumption during NSR process is given in Table A. Again, these results illustrate that ammonia is released when hydrogen is not fully consumed during the regeneration step of the NO<sub>x</sub>-trap catalyst.

**Table A:** Overview of the literature data for ammonia emission and hydrogen consumption during storage/reduction cycling experiments

Ref	Lietti <i>et al.</i> [29]	Lindholm <i>et al.</i> [19]	Pereda-Ayo <i>et al.</i> [26]	Castoldi <i>et al.</i> [12]	Breen <i>et al.</i> [23]	Bhatia <i>et al.</i> [16]	Kočí <i>et al.</i> [11]	Nova <i>et al.</i> [9]	Artioli <i>et al.</i> [13]	Choi <i>et al.</i> [27]
Catalyst	Pt-Ba(20) /Al	Pt-Ba(20.8) /Al	Pt-Ba /Al monolith	Pt-Ba(16-30) /Al	Pt(0.5)-Ba(16.4) /Al Pt(1.6)-Ba(13.8) /Al	Pt-Ba(13) /Al	Industrial	Pt-Ba(20) /Al	Pt-Ba(20) /Al	Industrial
T (°C)	100	400	260	350	350	370	250	200	350	200
H <sub>2</sub> inlet	2000 ppm	8000 ppm	0.85 %	2000 ppm	1.5 %	1500 ppm	3.3 %	2000 ppm	4000 ppm	3.4 %
H <sub>2</sub> outlet	80 ppm	not mentioned	traces	600-150 ppm	not mentioned	700 ppm	0.5 %	300 ppm	1000 ppm	1.4 %
NO inlet	1000 ppm	300 ppm	350 ppm	1000	300 ppm	500 ppm	500 ppm	1000 ppm	1000 ppm	300 ppm
NH <sub>3</sub> outlet	400 ppm	300 ppm	300 ppm	150-400 ppm	330-110 ppm	330 ppm	2200 ppm	180 ppm	500 ppm	120 ppm

The nature of the basic storage phase also affects the ammonia formation. For instance, the comparison of usual Pt-Ba/Al<sub>2</sub>O<sub>3</sub> catalyst with Pt-K/Al<sub>2</sub>O<sub>3</sub> sample (with similar molar amount of basic element, *i.e.* Ba or K) evidences a higher N<sub>2</sub> selectivity during the reduction step with H<sub>2</sub> of stored NO<sub>x</sub> over the K phase [10]. Authors report a similar reactivity for the H<sub>2</sub> + nitrate and NH<sub>3</sub> + nitrate reactions. In fact, on Pt-K/Al<sub>2</sub>O<sub>3</sub>, the onset for the direct H<sub>2</sub> + nitrate reaction leading to ammonia (step 1, Eq. 13) occurs at temperatures very close to the threshold for the NH<sub>3</sub> + nitrate reaction (step 2, Eq. 14), leading to the desired N<sub>2</sub> compound. It is then proposed that nitrogen formation occurs via a two step pathway. In agreement with Nova *et al.* [28], the stored NO<sub>x</sub> react preferentially with the introduced hydrogen to form NH<sub>3</sub> (step 1), whenever H<sub>2</sub> is present in the gas phase. NH<sub>3</sub> further reacts with stored NO<sub>x</sub> downstream to form N<sub>2</sub>, only in a hydrogen free environment (step 2) [2,20]. The selectivity towards NH<sub>3</sub> formation is governed by the relative constant rates of NH<sub>3</sub> formation and NH<sub>3</sub> consumption. In this dual-step mechanism, step 1 is much faster than step 2 [10,29], even though the characteristic reaction times for NH<sub>3</sub> formation and consumption are lower than the characteristic diffusion times of stored NO<sub>x</sub>. Finally, experimental results of literature can be summarized by scheme 2, as proposed by Clayton *et al.* [24]:



**Scheme 2.**

Simplified reaction network showing the conversion of H<sub>2</sub> and stored NO<sub>x</sub> to nitrogen-containing products (including N<sub>2</sub>O, N<sub>2</sub>, and NH<sub>3</sub>) [24].

This scheme comprises four pathways to N<sub>2</sub>O, NH<sub>3</sub> and N<sub>2</sub> formation occurring during the reduction of the stored NO<sub>x</sub> by H<sub>2</sub>. Especially, it is reported that possible mechanism includes

the activation of H<sub>2</sub> on Pt sites, as reported above. Then, nitrates adsorbed species are decomposed to NO<sub>x</sub> and released in the gas phase, due to hydrogen spill-over from the noble metal to the alumina support. NO<sub>x</sub> species are readily reduced to ammonia due to high H/N ratio locally attained.

The nature of the support, in terms of redox properties, obviously significantly modifies the ammonia rate formation, and consequently the ammonia selectivity during the regeneration step of the NSR process. We demonstrated [30] that NH<sub>3</sub> yield is significantly decreased over ceria-zirconia mixed oxides (Pt/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>), with a beneficial influence of the cerium content. With the increase in H<sub>2</sub> concentration in the rich pulses, it was confirmed that the ammonia selectivity decreases with the increase of the cerium content. In addition, manganese addition to a Pt/BaO/Al<sub>2</sub>O<sub>3</sub> model material (Pt/Ba(Mn)/Al catalyst) favours the NO<sub>x</sub> reduction by ammonia, especially at 400°C, even if the introduced hydrogen is not fully converted [1]. The study of the combined effect of Mn and Ce addition to model Pt/BaO/Al<sub>2</sub>O<sub>3</sub> catalyst is also reported [2]. A synergetic effect is highlighted between Mn and Ce when they are simultaneously added in Pt/BaO/Al<sub>2</sub>O. Significant decrease in ammonia emission in the 200-400°C temperature range is observed over these Mn-Ce doped materials. In addition to the enhancement of the NO<sub>x</sub> + NH<sub>3</sub> reaction rate, selective ammonia oxidation into nitrogen via the available oxygen at the catalyst surface is also advanced as a possible reaction pathway to explain the low NH<sub>3</sub> emission [31].

Finally, significant ammonia emission is possible at the NSR catalyst outlet. Two pathways are described, the direct route with H<sub>2</sub> and the isocyanate route with CO. However, the ammonia formation is especially favored in the presence of hydrogen, which can be produced *in situ* or upstream the NSR catalyst.

### 3. NH<sub>3</sub> storage and mechanism in NO<sub>x</sub> reduction over zeolite

Academic literature reporting the association of SCR and NSR catalysts essentially involves zeolite-based materials as SCR catalyst added in downstream position (see section 4). In the coupling NSR + SCR system, essentially ZSM5 zeolite was reported. This section is mainly focused on this zeolite-type structure. More specifically, an overview of the mechanistic aspect of NH<sub>3</sub>-SCR reactions and active sites of metal-exchanged zeolite catalysts is exposed.

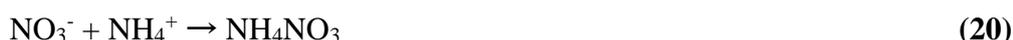
#### 3.1 NH<sub>3</sub> reactivity

Among the processes proposed to reduce NO<sub>x</sub> species in excess of O<sub>2</sub>, a key after-treatment technology is the on-stream reduction of NO<sub>x</sub> into N<sub>2</sub> and H<sub>2</sub>O over zeolite-based catalysts, using a NH<sub>3</sub> as reducer [32]. The reaction pathway of the NO<sub>x</sub> selective catalytic reduction with ammonia (NH<sub>3</sub>-SCR) is described by the following reactions (Eq 15-18):

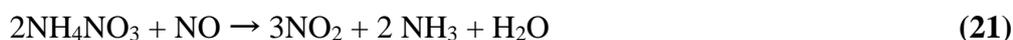


These reactions are usually denoted as “standard” (Eq. 15), “fast” (Eq. 16), “NO<sub>2</sub>-SCR” (Eq. 17) and “slow” (Eq. 18) SCR reactions [28,33,34,35,36]. It is usually established in the literature that SCR of NO<sub>x</sub> with NH<sub>3</sub> occurs through an Eley-Rideal type mechanism [37,38,39,40,41,42], in which adsorbed ammoniac reacts with weakly adsorbed NO or in the gas phase. Nevertheless, some studies suggest a reaction following a Langmuir-Hinshelwood mechanism [43,44,45]. It is reported in the literature that N<sub>2</sub> formation requires one nitrogen atom from a molecule of NO<sub>x</sub>, and a second nitrogen atom from ammonia molecule when reaction is performed over Fe/MFI [46]. This observation is consistent with SCR reactions described in Eq. 13-14. However, this mechanism requires firstly the NO oxidation into NO<sub>2</sub>, which is claimed to be the rate-determining step of the SCR mechanism [47]. The NO

oxidation step being rate determining, metal-exchanged zeolites present largely higher activity than transition metal free zeolite structures [48]. It is also clearly evidenced that the NO<sub>2</sub>/NO ratio is a key parameter for the SCR activity [34,49,50,51,52]. Indeed, fast SCR (Eq. 16) and NO<sub>2</sub>-SCR (Eq. 17) reactions are much faster than the standard NO-SCR reaction (Eq. 15). Transition metal centers are not only involved in NO oxidation. For instance, it is suggested that iron species also promotes the SCR reaction over zeolite framework in the case of the Fe-exchanged ZSM-5 materials [53]. Transition metal sites promote the formation of reactive nitrates on the catalyst surface in the presence of gaseous NO<sub>2</sub> [54]. In fact, the formation of intermediate Fe<sup>n+</sup>-NO species (n = 2, 3), Fe<sup>2+</sup>(NO)<sub>2</sub> complexes, and NO<sup>+</sup> are reported [55]. Nitrosyl ion (NO<sup>+</sup>) may be produced by N<sub>2</sub>O<sub>4</sub> disproportionation, which is firstly formed by NO<sub>2</sub> dimerization. NO<sup>+</sup> can further react with H<sub>2</sub>O to produce HNO<sub>2</sub>. HNO<sub>2</sub> can then react with ammonia to produce ammonium nitrite (NH<sub>4</sub>NO<sub>2</sub>), which decomposes quickly below 100°C, leading to the SCR products, N<sub>2</sub> and H<sub>2</sub>O [56]. Ammonium nitrate can also be formed (Eqs. 19-20):



In this later process, NH<sub>3</sub> is activated on zeolitic Brønsted acid sites, giving NH<sub>4</sub><sup>+</sup> ions [57]. This point is discussed below (section 3.2). Ammonium nitrate thereafter decomposes into NO<sub>2</sub> and NH<sub>3</sub>, as reported in Eq. 21:



The combination of reactions (18) and (20) leads to the “fast” SCR, as reported above (Eq. 16) [58].

However, if transition metal exchanged zeolites are active materials in NH<sub>3</sub>-SCR, N<sub>2</sub>O emission can be also observed. N<sub>2</sub>O emission however constitutes the main drawback of this system. For instance, Wilken *et al.* [59] reports a maximum N<sub>2</sub>O production at 200°C over

Cu-Beta zeolite. Mechanism of N<sub>2</sub>O emission is proposed to proceed through the decomposition of ammonium nitrates (Eq. 22):



Fast SCR conditions, and more especially high NO<sub>2</sub> concentrations, are also proposed to favor the N<sub>2</sub>O formation at low temperature (*i.e.* T ≤ 350°C) [60] (Eq. 23). Mechanism involving NO (Eq. 24) is proposed to occur at higher temperature (*i.e.* T ≥ 350°C) [61].



### 3.2 Active sites, zeolite framework and acidic properties

In the NH<sub>3</sub>-SCR mechanism, ammonia is firstly adsorbed and activated as NH<sub>4</sub><sup>+</sup> ions on the Brønsted acid sites of the zeolite framework. Acidic properties are then a crucial factor that determines the SCR activity. Since zeolite acidity is affected by the Si/Al ratio, high Al contents in the framework are favorable to achieve high NO<sub>x</sub> conversions. Indeed, the Brønsted acid sites of the zeolite structure originate from aluminum centers [60,62]. Besides, it seems that zeolite with small average pore diameter, as encountered in MFI, MOR, BEA or FER materials, are the more active for NH<sub>3</sub>-SCR reaction. In opposition, molecular sieves having larger pore size, including Y, USY or MCM-41 structures, exhibit lower activities. It is proposed in the literature that the formation of an active complex [NH<sub>4</sub><sup>+</sup><sub>x</sub>][NO] (with x = 1, 2) during SCR is facilitated in small pores, without effect of reactant surface mobility [63,64]. A second hypothesis to explain the differences observed with the pore size is the formation of higher concentrations of 3H-NH<sub>4</sub><sup>+</sup> compound (NH<sub>4</sub><sup>+</sup> bonded to three hydrogen atoms) in small pore size support [65]. 3H-NH<sub>4</sub><sup>+</sup> compound is also reported as necessary for the formation of the active [NH<sub>4</sub><sup>+</sup><sub>x</sub>][NO] complex during the NH<sub>3</sub>-SCR reaction. In addition, the zeolite channels size can also influence the H-bonding with framework oxygen atoms [64]. For instance, FeY and FeMCM-41, with large pore sizes, show lower activities for NH<sub>3</sub>-SCR than

FeZSM-5.

Nevertheless, it is also proposed that the active sites for the SCR of NO by ammonia over HZSM-5 are highly acidic extra-framework alumina. In opposition, for NO<sub>2</sub> reduction reaction, both framework and extra-framework alumina sites are suggested to be active sites [66].

On the basis of these results, it seems that the activity of zeolite materials is associated with two main properties [67]:

1. A shape selectivity effect, due to the molecular sieving properties associated with the well defined crystal pore sizes, in which a part of the catalytic active sites are located;
2. A strong Brønsted acidity of bridging Si–(OH)–Al sites, generated by the presence of aluminum inside the silicate framework.

However, Brandenberger *et al.* [68] evaluated the selective catalytic reduction of NO with NH<sub>3</sub> over different Fe-ZSM-5 samples at equal exchange degree but different Brønsted acidities. This study reveals that the acidity of the catalyst is not a crucial factor to achieve high activity. Brønsted acidity may not be required for the adsorption or activation of the ammonia molecule, but it is necessary to bind and disperse the transition metal ions. The form in which ammonia is adsorbed on the support is consequently not crucial. These observations are confirmed by Schwidder *et al.* [69]. Indeed, high reaction rates for the NH<sub>3</sub>-SCR can be achieved with non-acidic catalysts. A promoting effect of acidity is noted for the catalysts that contain the iron in the most favorable structure (*i.e.* oligomeric Fe oxo clusters).

In fact, characterization of the ZSM-5 acidic properties shows that two types of hydroxyl groups are mainly detected. Using FT-IR characterization, these two types are characterized by bands at 3720 and 3605 cm<sup>-1</sup> [70]. Thermal activation temperature strongly affects acidic properties. By increasing the temperature, dehydroxylation of the zeolite is observed above

400°C. The dehydroxylation results in a decrease of the number of Brønsted acid sites, while an increase in strong Lewis acid sites is observed. The dehydration at high temperature irreversibly removes the more acidic hydroxyl groups. Dealumination of zeolitic framework is also reported to modify acidity. Ammonia adsorption and temperature programmed desorption over ZSM-5 (Si/Al=11.8) is studied in Ref. [71]. Three different states of chemisorbed ammonia are distinguished, which show desorption peaks at around 80°C, 180°C and 430°C. The distribution of chemisorbed ammonia is also reported as a function of catalyst pre-treatment or deactivation. Recently, it was proposed that adsorption of ammonia on Brønsted acid sites goes through co-adsorption of up to four ammonia molecules on one active site at low temperatures. In addition, only a fraction of the aluminum framework is evidenced to be able to bind ammonia as ammonium ion [72]. Consequently, the support can act mainly as a reservoir for ammonia molecules, which then migrate to the active sites in order to undergo the reaction with NO<sub>x</sub>.

Iron and copper are the main active species proposed in zeolites. Although the identity and nuclearity of active sites is still in debate, Cu-zeolite binuclear species are clearly reported as active sites. Nevertheless, it seems that copper active site nature is strongly influenced by the reaction temperature and dependant on the zeolite used and its properties. Indeed, over FAU zeolite, [CuOCu]<sup>2+</sup> dimer species are proposed to catalyze NH<sub>3</sub>-SCR reaction at low temperature ( $T \leq 300^\circ\text{C}$ ) [73]. To the opposite, Cu<sup>2+</sup> is suggested to become active at higher temperature ( $T \geq 350^\circ\text{C}$ ) over NaY [74,75]. The active sites in iron supported zeolites seem to have different natures. In Fe/ZSM-5 (Fe/Al=1), EXAFS characterization reveals the presence of diferric (hydr)oxo-bridged binuclear clusters, located at the ion-exchange positions of the zeolite, and compensating one or two lattice charges [76,77]. For Fe/Al=0.8, iron is predominantly present as large hematite particles, although a minor fraction of binuclear species might be present as well [76]. Small Fe<sub>x</sub>O<sub>y</sub> clusters like Fe<sub>4</sub>O<sub>4</sub>, isolated Fe<sup>2+</sup> and Fe<sup>3+</sup>

ions, are also reported as possible active sites in the literature [78,,81]. Besides, electron-deficient ferric oxide nanoclusters, isolated iron ions, and possibly oxygen-bridged iron binuclear complexes, may likewise coexist in Fe/MFI active catalysts [82]. Finally, a high exchange level (M/Al ratio  $\approx 1$ ), which can be achieved with the CVD method for instance, confers activity at low temperature for the material. Additionally, a high metal content may lead to extra-framework metal oxide clusters, which can exhibit high activity for  $\text{NH}_3$  oxidation [81].

Other catalytic systems are also studied for the abatement of  $\text{NO}_x$  by reaction with ammonia, namely vanadium oxide - titania based samples or transition metal oxide - based materials. On these catalysts, ammonia is activated by coordination over Lewis acid sites and can react with gas phase or weakly adsorbed  $\text{NO}$  [48]. Over  $\text{V}_2\text{O}_5\text{-WO}_3(\text{MoO}_3)/\text{TiO}_2$  materials, new relevant contributions appeared in the literature, in particular concerning the reaction mechanism and the role of preoxidation of  $\text{NO}$  to  $\text{NO}_2$ . Coordinated ammonia would be oxidized to amide species, which later reacts with  $\text{NO}$  to form adsorbed nitrosamide specie. Nitrosamide specie decomposes into nitrogen and water, while oxygen reoxidizes the catalyst surface [83]. Unfortunately, these catalytic systems remain poorly active at low temperature, and relatively high temperature ( $T \geq 350^\circ\text{C}$ ) is needed to achieve high  $\text{NO}_x$  abatement. In order to increase the low temperature activity, new formulations based on transition metal oxides are proposed. For instance, Mn and Fe oxides supported on titania and alumina are active in  $\text{NH}_3\text{-SCR}$  at low temperature ( $150\text{-}250^\circ\text{C}$ ) [84]. However, the main drawback of these catalysts is the limited selectivity of  $\text{NO}_x$  conversion into  $\text{N}_2$ , and the significant production of  $\text{N}_2\text{O}$ . In addition, vanadia-based catalysts are not suitable for high temperature application as it can be the case in automotive exhaust pipe. Indeed, the sublimation of  $\text{V}_2\text{O}_5$  occurs from  $650^\circ\text{C}$  [85,86]. Then, new catalytic systems, having high efficiency at low temperature, thermally stable up to  $800^\circ\text{C}$  and with a limited impact of the  $\text{NO}_2/\text{NO}_x$  ratio on the activity, are

developed. Amongst these new emerging SCR catalytic systems, acidic zirconia mixed-oxides are described as attractive alternatives [87]. For instance, 50% NO conversion was attained at 250°C for the standard SCR process. By applying the “fast” SCR conditions ( $\text{NO}_2/\text{NO}_x = 50\%$ ), 97% of  $\text{NO}_x$  were reduced to  $\text{N}_2$  at only 200°C [88]. The promotion of acidic zirconia by ceria also increases the  $\text{NO}_x$  conversion, the selectivity to  $\text{N}_2$  and the catalyst durability. These results show that modified acidic zirconia oxides are attractive materials for Diesel after treatment systems [87].

However, Fe or Cu exchanged zeolites, which exhibit high reactivity toward the  $\text{NO}_x$  SCR by  $\text{NH}_3$ , are the more quoted materials for a coupling with a NSR catalyst.

#### **4. Coupling of $\text{NO}_x$ trap and $\text{NH}_3$ -SCR catalysts**

##### *4.1. Emergence and development of the NSR-SCR coupling concept*

The concept of adding a  $\text{NH}_3$  adsorbing materials to a  $\text{NO}_x$  reduction catalyst was patented by Toyota in 1998 for applications on gasoline engines [89]. In the claimed configuration, a Cu-ZSM-5 catalyst is added to the three way catalyst (TWC) with the engine working in cycling conditions. In rich conditions,  $\text{NO}_x$  can be reduced to  $\text{N}_2$  and  $\text{NH}_3$  which can be stored on the zeolitic materials. When the engine turns to lean conditions,  $\text{NO}_x$  is no longer reduced on the TW catalyst. Ammonia is in part oxidized (to  $\text{N}_2$ ) or desorbed. It may then react with NO passing through the TW monolith. This initial system was improved by introducing a small, auxiliary engine working in rich conditions and able to produce ammonia needed for reduction of the  $\text{NO}_x$  issued from the main engine [90]. Exhaust pipes are arranged to receive a TWC catalyst and a  $\text{NH}_3$  adsorbing materials. In a further patent, Toyota claimed a new embodiment of the concept in which a group of cylinders are working in rich conditions while the others are working in lean conditions [91]. TW catalysts and  $\text{NH}_3$  adsorbing and oxidizing catalysts ( $\text{NH}_3$ -AO) are interconnected to receive alternatively the gases issued from the first

and second groups of cylinders. The patent claims a wide range of  $\text{NH}_3$ -AO catalysts: zeolites, silica-alumina, titania doped with Cu, Fe, Cr,... This last system was finally improved by replacing the TW catalyst by a  $\text{NO}_x$ -trap materials (named  $\text{NO}_x$ -occluding and reducing catalyst,  $\text{NH}_3$ -OR in the patent) [92]. In this configuration, the system is very close to the NSR-SCR coupling for  $\text{NO}_x$  after-treatment. Several systems associating NSR and SCR catalysts were further claimed in Toyota patents [93,94].

A system including an ammonia generating catalyst coupled with the  $\text{NO}_x$ -trap or a TW catalyst was claimed by Daimler-Chrysler in 2002 under the name of "smart catalytic converter" [95]. In the lean operating phases, the nitrogen oxides are intermediately stored in the nitrogen oxide adsorption catalyst. In the rich operating phases, ammonia is generated by the ammonia generating catalyst from the nitrogen oxides contained in the exhaust gas. The generated ammonia then causes a nitrogen oxide reduction in the nitrogen oxide adsorption catalyst. The mechanism by which ammonia is generated is obviously not detailed. The patent merely supposes that ammonia can be formed by reaction of  $\text{NO}_x$  with reducers in excess (especially  $\text{H}_2$ ) during the rich operating phases. The materials catalyzing the reaction between NO and ammonia is not fully described. It is suggested that the SCR reaction can occur on the  $\text{NO}_x$  adsorbing catalyst. Commercially, the system was implemented on the Mercedes E320 Bluetec vehicle in 2007.

The coupling between a  $\text{NO}_x$ -trap sample and a  $\text{NH}_3$ -SCR catalyst, located downstream the first one or in a double layer on the monolith, was patented by Ford in 2004 [96]. In this patent application, ammonia is generated during the rich spike of the NSR catalyst cycle. It is stored on the SCR catalyst and further used to reduce  $\text{NO}_x$  during the lean phase. Depending on the temperature, a significant fraction of the nitrogen oxides may not be trapped and passes through the NSR catalyst: the SCR catalyst having stored ammonia helps at converting the  $\text{NO}_x$  not stored on the NSR catalyst. The Ford patent claims a NSR catalyst composed of

noble metals deposited on a NO<sub>x</sub>-trap materials (alkali, alkali earth metals,...) while the SCR catalyst would be made of zeolite, silica-alumina or titania promoted by Cu, Fe or Ce. This system was further detailed in a patent in 2008 [97]. The coupling between a NSR and a SCR catalyst was also claimed by Engelhardt [98]. A more general system in which the SCR catalyst could be coupled to NSR and oxidation catalysts and associated with a soot filter was patented by BASF [99]. In this patent, the claimed SCR catalyst is composed of silver tungstate Ag<sub>2</sub>WO<sub>4</sub> supported on alumina. Another BASF patent was published in 2010 to cover the specific case of NSR-SCR coupling system [100]. A NSR-SCR coupling system was also depicted by Johnsson-Matthey [101]. Indeed, recently Twigg et al. suggest the development of a multi component diesel catalyst known as “four-way catalysts” (FWCs) [102]. SCR and/or NO<sub>x</sub>-trapping components will be incorporated into catalysed filters from diesel cars in order to be cost-effective, weight effective and space-effective.

#### *4.2. Coupling of Pt(RhPd)/BaO/Al<sub>2</sub>O<sub>3</sub> with Cu-zeolite catalysts*

The NSR-SCR coupling was studied by Shinjoh et al. who used Cu-ZMS-5 as the SCR catalyst [103]. The complete system comprises three catalysts: Pd/γ-Al<sub>2</sub>O<sub>3</sub>, NSR (Pt-Rh/BaO/Al<sub>2</sub>O<sub>3</sub>) and Cu-ZMS-5 (5%Cu). The catalyst performances were compared in lean/rich cycled conditions (3 min each). A significant beneficial effect of adding Cu-ZMS5 to the Pd+NSR catalyst was observed between 230 and 310°C (+15% conversion of NO<sub>x</sub> when Cu-ZSM-5 is added). In the rich phase, Pd could increase the production of ammonia further stored by the SCR catalyst (the NSR catalyst alone would produce less ammonia). In the lean phase, Pd would improve the oxidation of NO to NO<sub>2</sub>.

The effect of Cu-ZSM-5 (5%Cu) addition on the performances of Pt-Rh/BaO/Al<sub>2</sub>O<sub>3</sub> (Pt-RhBa) catalyst was also investigated by Corbos et al. [104,105]. The catalytic system was tested in periodic cycling conditions (100 s lean/10 s rich) between 200 and 400°C in three

configurations: NSR catalyst alone, physical mixture of NSR + CuZSM-5 or dual bed catalyst (CuZSM-5 downstream NSR). The results are shown in Table B.

While Cu-ZSM-5 is almost inactive in NO<sub>x</sub> abatement in NSR cycling conditions, addition of this catalyst to Pt-Rh/Ba improves the performance of the NSR catalyst at 250 and 300°C. The greatest effect of Cu-ZSM-5 is observed in the presence of H<sub>2</sub> in the reductant mixture. This is in line with H<sub>2</sub> giving the highest yield of ammonia in NSR cycling conditions (see section 2). Interestingly, the physical mixture of Pt-Rh/Ba and CuZSM-5 gives better performances than the dual bed system. Corbos et al. concluded that a close proximity of the NSR catalyst with the NH<sub>3</sub>-SCR catalyst was required for a better production and use of ammonia produced during the rich phase. However, most experiments were carried out in absence of water in the synthetic gas. Adding 1% H<sub>2</sub>O in the gas mixture did not cause great difference in NO<sub>x</sub> removal over the NSR catalyst alone while a slight decrease in activity of the NSR-SCR catalyst combination was observed.

**Table B:** Effect of adding a SCR catalyst (Cu/ZSM5) to a NSR catalyst (Pt-Rh/Ba) in cycling conditions: 100 s lean (500 ppm NO + 0.13% CO/H<sub>2</sub> + 167 ppm C<sub>3</sub>H<sub>6</sub> + 1% CO<sub>2</sub> + 10% O<sub>2</sub> in He) and 10 s rich (100 ppm NO + 8.53% CO/H<sub>2</sub> + 1% CO<sub>2</sub> in He). The gas mixture CO/H<sub>2</sub> contains 75% CO and 25% H<sub>2</sub>. Entry 2; results with pure CO.

Entry	Catalyst	NO <sub>x</sub> removal		
		250°C	300°C	400°C
1. With H <sub>2</sub>	Pt-Rh/Ba (NSR alone)	39	50	39
	CuZSM-5	11	13	-
	Pt-Rh/Ba + CuZSM-5 (2 beds)	46	61	37
	Pt-Rh/Ba + CuZSM-5 (phys. mix.)	86	79	38
2. Without H <sub>2</sub>	Pt-Rh/Ba (NSR alone)	39	43	36
	Pt-Rh/Ba + CuZSM-5 (2 beds)	39	58	-
	Pt-Rh/Ba + CuZSM-5 (phys. mix.)	54	66	-

A similar system (Pt-Rh NSR + Cu-zeolite) was recently investigated by Wang et al. [106] of University of Kentucky and Ford Motor Company. However, using a CO+H<sub>2</sub>+C<sub>3</sub>H<sub>6</sub> mixture as the reductant in cycling experiments, NO<sub>x</sub> conversion was higher than with ammonia alone.

Wang et al. concluded that propene was an efficient reducer in the NSR-SCR combination. Separate experiments proved that Cu-zeolite was a good catalyst for NO<sub>x</sub> reduction, both by ammonia and alkenes. High resistance to deactivation by hydrocarbon and sulphur was obtained with a new generation of Cu-zeolite (Cu-CHA) [107,108]. The NSR-SCR system is more efficient than the NSR catalyst alone up to 425°C. Above this temperature, the SCR catalyst has no effect and it is advantageous to increase the loading of the NSR catalyst. However, such high temperatures are rarely encountered with normal diesel engine free of particulate filter.

#### *4.3. Coupling of Pt(RhPd)/BaO/Al<sub>2</sub>O<sub>3</sub> with Fe-zeolite catalysts*

Systems coupling NSR with Fe-zeolite SCR catalysts were studied by many authors, in particular the Group of Forzatti in Milano [109-111], the Group of Daimler AG [112-115] and others [116-118].

Kinetic studies, specific experiments with designed reactants coupled to FTIR or DRIFT were mainly employed by the Group of Milano to get detailed information about the behavior of each of the catalysts (Pt-Ba/Al<sub>2</sub>O<sub>3</sub> and Fe-ZSM-5). As expected, NO<sub>x</sub> is mainly stored on the basic NSR catalyst while ammonia formed upon the rich phase is mainly stored on the acidic SCR catalyst. Gaseous NO<sub>x</sub> slipped from during the lean phase reacts with NH<sub>3</sub> stored on Fe-ZSM-5 to give N<sub>2</sub>. This classical view of the NSR-SCR system can lead to different performances depending on the proximity of the NSR and SCR catalysts and on the presence or not of CO<sub>2</sub> and H<sub>2</sub>O in the gas mixture. Table C summarizes the result of Castoldi et al. [111]. Prolonged rich and lean phases (40 min each) were carried out with intermediary He purges to have a clearer analysis of the compounds stored and formed during each phase. Adding the SCR catalyst has a significant positive effect on the NO<sub>x</sub> removal, in the presence and in the absence of CO<sub>2</sub> and water in the gas mixture. This effect is slightly more marked

when both catalysts are physically mixed, which is in line with the results of Corbos et al. [104]. However, though the dual bed system seems less effective for NO<sub>x</sub> removal, it leads to a higher selectivity to N<sub>2</sub> in rich phase, when there is no CO<sub>2</sub> and H<sub>2</sub>O and in both phases (lean and rich) in the presence of CO<sub>2</sub> and H<sub>2</sub>O.

The results of Tables C and D were obtained at 250°C. In the physical mixture, the amount of removed NO<sub>x</sub> decreases with the temperature in absence of CO<sub>2</sub> and H<sub>2</sub>O while it is almost constant with CO<sub>2</sub> and H<sub>2</sub>O. At 350°C, there is virtually no difference when there is CO<sub>2</sub>+H<sub>2</sub>O or not in the gases. In the dual bed, the amount of removed NO<sub>x</sub> tends to increase with temperature in every cases (with CO<sub>2</sub>+H<sub>2</sub>O or not).

**Table C:** Quantitative analysis of lean/rich experiments performed over the NSR, NSR + SCR physical mixture and NSR/SCR dual bed configurations in the absence of CO<sub>2</sub> and H<sub>2</sub>O. Experimental conditions: T = 250°C; lean phase NO (1000 ppm) in O<sub>2</sub> (3% v/v) + He; rich phase H<sub>2</sub> (2000 ppm) in He; catalyst weight 60 mg LNT (or 60 mg NSR + 60 mg SCR); total flow rate 100 Ncm<sup>3</sup>/min mol/gcat refers to NSR Pt–Ba/Al<sub>2</sub>O<sub>3</sub> weight. From ref. [111].

Amounts (μmol/gcat)	NSR alone	NSR+SCR (phys. mix)	NSR + SCR (dual bed)
NO <sub>x</sub> removed (a)	429	512	472
NO <sub>x</sub> stored(a)	429	434	423
N <sub>2</sub> (lean)	0	78	49
N <sub>2</sub> (rich)	193	51	209
NH <sub>3</sub> slip	57	70	14

**Table D:** Same results with 0.1 % CO<sub>2</sub> and 1% H<sub>2</sub>O in the gas mixture (lean and rich). Other conditions are given in Table C. From ref. [111].

Amounts (μmol/gcat)	NSR alone	NSR+SCR (phys. mix)	NSR + SCR (dual bed)
NO <sub>x</sub> removed (a)	272	323	396
NO <sub>x</sub> stored(a)	272	307	272
N <sub>2</sub> (lean)	0	16	123
N <sub>2</sub> (rich)	93	21	135
NH <sub>3</sub> slip	117	7	0

Following the publication of patents (see section 4.1), the Group of Daimler AG essentially worked at rationalizing the concept of smart catalytic converter by modeling the NSR-SCR

dual bed [113,114]. It was shown that a good adjustment of the NSR and SCR catalyst volume as well as a good balance between rich and lean cycle lengths are a prerequisite to an optimal operation of the system. An example of the modeling results, taken from ref. [112], is given in Table E. The model shows that increasing the SCR-to-NSR volume ratio (keeping constant the total volume) leads to a slight increase of the % of NO<sub>x</sub> removal and to an increase of the amount of reacted ammonia (100% in the second configuration of Table E). The same model (COMSOL package) was used to optimize the lean/rich cycle duration.

**Table E:** NO<sub>x</sub> removal efficiency and percentage of ammonia used to reduce NO<sub>x</sub> in a smart catalytic converter based on Pt-Ba-NSR and Fe-zeolite SCR catalyst. Reaction conditions: 240°C, 165s lean (500ppm NO + 8%O<sub>2</sub> + 8%CO<sub>2</sub> + 8%H<sub>2</sub>O), 7s rich (500ppm NO + 1.6%O<sub>2</sub> + 1.4%H<sub>2</sub> + 0.3%C<sub>3</sub>H<sub>6</sub> + 4.2%CO + 11.5%CO<sub>2</sub> + 8%H<sub>2</sub>O). From ref. [112].

Catalyst configuration. Respective volumes	% NO <sub>x</sub> removed on the NSR unit	% NO <sub>x</sub> removed on the SCR unit	NH <sub>3</sub> reacted/ NH <sub>3</sub> adsorbed
2V of NSR + 1V of SCR	55	7	0.3
1V of NSR + 2V of SCR	48	15	1.0

Another modeling of the reactor volume was performed by Seo et al. [119] with a special insight to the formation of N<sub>2</sub>O. In the NSR-SCR coupling, it is important to minimize (or annihilate) both ammonia and N<sub>2</sub>O in the aftertreatment exhaust gas. This means that ammonia should be used to reduce NO<sub>x</sub> (or be oxidized to N<sub>2</sub>) while N<sub>2</sub>O, if formed, should be destroyed in the catalytic system. The NSR catalyst was composed of Pt/Pd/Rh/Ba/Ce/Zr on Al<sub>2</sub>O<sub>3</sub> (relative weight-%: 3.3/0.72/0.31/12.56/7.97/4.49) while the SCR catalyst was a Fe-TMI zeolite (1.8 % Fe). Although it is not the best configuration in terms of NO<sub>x</sub> abatement, the system with an equal volume of NSR and SCR catalysts shows the best result in terms of ammonia and N<sub>2</sub>O slip. A similar configuration was adopted by Pereda-Ayo to study the NSR (Pt-Ba-Al<sub>2</sub>O<sub>3</sub>)-SCR (Fe-BEA zeolite) coupling. Nine values of nine parameters (81 experiments) were chosen to construct the abacus for predicting optimal performances. Very critical points are the temperature, the duration of lean-rich cycles and the concentration of H<sub>2</sub>

in the respective lean and rich phase. It was shown that there is an optimum value of  $H_2$  concentration (3% in the conditions of ref. [118]) to get the highest  $NO_x$  conversion and the complete use of the ammonia produced in the NSR catalyst (no  $NH_3$  slip). The specific role of  $H_2$  concentration was also investigated by Lindholm et al. [116] who showed that the optimum  $H_2$  concentration depended on the process temperature. A higher hydrogen concentration enhances the  $NO_x$  removal efficiency at lower temperatures while this concentration should be reduced at higher temperatures to avoid an excess of ammonia leading to inhibition of the SCR reaction. Lindholm also showed that the  $NO_2/NO$  ratio was a critical factor in the NSR-SCR coupling. There is a clear benefit when  $NO_2$  is present in the feed at low temperatures.

#### *4.4. Other systems*

Sullivan and Keane have proposed a system in which both NSR and SCR components are included in the same materials [120]. Ba-ZSM-5 (4.3%Ba), Fe-ZSM-5 (0.8 % Fe) and Ba-Fe-ZSM-5 were studied to evaluate the benefit of the concept. Oxygen is required to desorb  $NO_x$  previously adsorbed on the catalyst, while gaseous ammonia is able to react with this stored  $NO_x$ . Interestingly, Sullivan and Keane showed that  $N_2O$  was produced in the  $NH_3(g)/NO(a)$  reaction on Ba-ZSM-5 and Fe-ZSM-5, but to a lesser extent on the composite FeBa-ZSM-5 catalyst.

Corbos et al. investigate the coupling of Pt-Rh/Ba/ $Al_2O_3$  with different potential SCR catalysts (Co/ $Al_2O_3$ , CuZSM-5, Ag/ $Al_2O_3$ ) [105]. As expected (and already found in a previous work [104], addition of Cu-ZSM-5 gave the highest performances. Excellent performances were also obtained with Co/ $Al_2O_3$  while addition of Ag/ $Al_2O_3$  had no significant influence. The negative effect of water on the global performances of Pt-

Rh/Ba/Al<sub>2</sub>O<sub>3</sub>+ Cu-ZSM-5 was ascribed to an inhibition of the reactions occurring on Cu-ZSM-5.

Finally the work of Kim et al on the HC-SCR and NH<sub>3</sub>-SCR coupling should be mentioned [121]. Although this study is out of the scope of the present review, it obeys to the same principle: the first bed (composed of Ag/Al<sub>2</sub>O<sub>3</sub>) is active in NO<sub>x</sub> reduction by hydrocarbons or alcohols but it produces also ammonia and HCN which is used in the second bed (CuCoY or Pd/Al<sub>2</sub>O<sub>3</sub>) to reduce the unconverted NO<sub>x</sub> by ammonia.

## **5. Conclusion and perspective**

The combination of NO<sub>x</sub> trapping materials with NH<sub>3</sub>-SCR catalysts for the NO<sub>x</sub> treatment from mobile lean-burn engines has been investigated. Particular attention has been paid in mechanism of ammonia emission and reactivity towards NO<sub>x</sub> abatement in NSR process. For the first point, two reaction paths are proposed in literature. In presence of hydrogen during the rich pulses of the LNT regeneration, ammonia can be formed by direct reaction with the previously stored NO<sub>x</sub>. When CO is use as the reducer agent, water-assisted reaction, by hydrolysis of intermediate isocyanate species, is suggested. In presence of water and carbon dioxide in the gas mixture, both reaction pathways co-exist due to direct and reverse water gas shift reaction. Ammonia is thereafter involves in the NO<sub>x</sub> reduction mechanism, by a sequential route in which NH<sub>3</sub> reacts faster with NO<sub>x</sub> to yield N<sub>2</sub> compared with its own formation rate. It is found that both the nature and the content of the basic element as well as the redox properties of the support interfere in NH<sub>3</sub> yield.

Ammonia may likewise be used as reducer for selective catalytic reduction of NO<sub>x</sub> species. For this application, metal-exchanged zeolite catalysts offer new opportunities to reduce NO<sub>x</sub> emissions from lean-burn engine via the NH<sub>3</sub>-SCR process. Iron-exchanged ZSM-5 has received much attention because of its promising activity and stability in the NH<sub>3</sub>-SCR process. Correlating catalytic activities with the concentration of mononuclear and binuclear

Fe species shows that both types of Fe ions and even small metal clusters are active sites for SCR, but that isolated species are more active. The topology of the zeolite is also an important factor, as well as its stability under hydrothermal conditions. A high exchange level (M/Al ratio  $\approx 1$ ) seems to be proscribed creating extra-framework metal oxide clusters, which can be highly active for NH<sub>3</sub> oxidation.

The coupling between a NO<sub>x</sub>-trap catalyst and a NH<sub>3</sub>-SCR material, located downstream the first one or in a double layer on the monolith, was firstly patented by Ford in 2004. In other recent studies, two main SCR catalysts are usually associated in such system, namely Cu-ZSM-5 and Fe-ZSM-5 catalysts. For instance, it is reported that using Cu-ZSM-5 material, about 15% to 50% of supplementary NO<sub>x</sub> conversion can be achieved, depending on the working conditions. Whatever the zeolite used, higher performances are reported with H<sub>2</sub> as reducers, since it enhances NH<sub>3</sub> formation in the first NSR catalytic bed. Physical mixture of NSR and SCR catalysts gives better performances than dual bed system. It is concluded that a close proximity of both materials was required for a better use of ammonia produced during the rich pulses.

Finally, in almost every case of lean-burn engine after-treatment implementation in the US and Europe, a Diesel particulate filter (DPF) is required. The NSR + SCR system must be compatible with the DPF working mode. Filter regeneration induces severe exotherms (900-1000°C) which expose NSR + SCR catalysts to harsh environment. To maintain the durability of this coupled system, the catalysts must exhibit high thermal stability. As a consequence, usual vanadia-based oxides SCR catalysts are not suitable. The stability of metal-exchanged zeolite has to be improved to prevent potential metal migration, or sulfur poisoning. A way is metal-exchanged in small-pore zeolites which shown to be much more hydrothermally stable than the medium-pore zeolite. New acidic zirconia-based oxides seem also attractive for this application.

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