An overview of the production and use of ammonia in NSR + SCR coupled system for NO_x reduction from lean exhaust gas.

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Abstract

This paper gives a critical overview of the recent advances in NO_x abatement in excess of oxygen based on the combination of the NO_x storage-reduction (NSR) and Selective Catalytic Reduction (SCR) processes. Ammonia may be produced during the regeneration step of NSR catalyst, by the direct reaction ($\text{NO}_x + \text{H}_2$) or/and the isocyanate route. Recent literature highlights that the ammonia production rate is higher than the ammonia reaction rate with the remaining NO_x in order to form N₂. In order to optimize the use of the *in situ* produced ammonia, a catalyst dedicated to the NO_x-SCR by NH₃ can be added. Zeolites are the main studied materials for this application. Catalytic reduction of NO_x by NH₃ relates a complex mechanism, in which the nuclearity of the active sites is still an open question. Over zeolites, the NO to NO₂ 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 NH₃-SCR material to the NSR catalyst is a possible way to increase the global NO_x abatement and maximize the N₂ selectivity, together with the prevention of the ammonia slip.

Keywords: NO_x; NSR; SCR; ammonia; NH₃.

1. Introduction

In order to reduce CO₂ 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_x abatement in the post combustion catalytic converters. Two catalytic solutions are envisaged to be implemented on those types of cars: (i) the NO_x Selective Catalytic Reduction by NH₃ (NH₃-SCR) or (ii) the NO_x-trap system (also called NO_x-Storage Reduction or NSR system). Today in Europe, the NH₃-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_x-trap catalyst contains a noble metal (Pt) allowing the NO oxidation into NO₂, a basic phase (Ba oxide/carbonate) for trapping NO₂ 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_x 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 H₂ 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 H₂) reduce the desorbed NO_x 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_x abatement and the N₂ selectivity, adding a NH₃-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_x passing through the NO_x-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_x reduction.

2. NH₃ emission from NSR catalysts

The NO_x storage reduction (NSR or Lean NO_x 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_x storage phase. It works mainly in lean condition. NO_x 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 N₂ on the precious metals [6,7]. The nature of the reducers in the rich mixture directly impacts the NO_x conversion and the selectivity of the NSR reaction. On usual NSR model catalysts, namely Pt/(BaO)/Al₂O₃, hydrogen is reported to be more efficient as reducing agent than CO [8,9]. This higher efficiency of H₂ 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_x with hydrogen (Eq. (1.0)) [10,11]. This route is likewise reported in Ref. [12] over Pt-Ba/Al₂O₃ material, when H₂ is used as the reducer. Artioli *et al.* [13] observed that, depending on the gas feed composition, ammonia is emitted together with CO₂ 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_x is initially fully selective into nitrogen, according to the Eqs. (2).

The catalyst temperature is also an important parameter, impacting the NO_x 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 H₂ also reacts with remaining oxygen (from gas phase and/or catalyst), leading to an additional release of stored NO_x. 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 N₂ 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 H₂ 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_a, Eq. 4), remaining on the Pt surface from the reduction of NO₂. In Eq. 4, Pt* denotes reduced Pt sites.

The so produced H₂O destabilizes the adsorbed nitrates. Consequently, surface nitrates present over alumina are suggested to be decomposed on the Pt free surface. The dissociation of NO_x species on the Pt clusters can be followed by the recombination of N_a atoms to form N₂ (Eq. 5 and 6), or by the reaction of these N_a atoms with H₂ to form NH_x and, ultimately, NH₃.

In this process, the primary role of H₂ is to keep the platinum surface clean and reduced for

the NO_x dissociative adsorption. Indeed, the reaction of H₂ with O_a leads to the production of H₂O and free Pt⁰ surface site (Eq. 4). It is suggested that the H₂ dissociative adsorption, leading to H_a species, promotes the NO dissociation reaction on Pt surface [15]. Structure and temperature are also key parameters for the NH₃ emission. Indeed, modeling the effect of platinum dispersion of a model Pt/BaO/Al₂O₃ sample, allowed Bhatia *et al.* [16] to propose that highest amount of NH₃ is produced over low dispersed catalyst (3.2% platinum dispersion) at high temperature ($T \geq 300^{\circ}\text{C}$). Effect of temperature in NH₃ formation is important since it was also observed that ammonia formation is enhanced at low temperature ($T \leq 200^{\circ}\text{C}$) 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_x and the platinum sites. Proximity between storage sites and reaction sites affects the stored NO_x transport process [17].

Ammonia can also be formed via the isocyanate route, when CO is used as the main reducer [8]. At low temperature ($T < 150^{\circ}\text{C}$), the first reaction is the removal of adsorbed oxygen atoms over the Pt particles (Pt...O_a), leading to CO₂ production (Eq. 7).

The obtained free Pt sites become available for the CO adsorption step as for the NO_x 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 CO₂ formation occur at the expense of adsorbed nitrate species, while N₂ is not produced. At higher temperatures ($T > 300^{\circ}\text{C}$), these NCO species can readily react with the stored NO_x. This reaction route eventually leads to the consumption of both nitrate and NCO adsorbed species (Eq. 9).

It is reported that N₂ 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 NH₃ and CO₂ (Eq. 10 and 11).

The presence of H₂O and CO₂ 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 H₂ in gas phase, even if the initial reducer in the rich mixture is H₂ 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_x 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_x removal. In opposition, the presence of CO₂ leads to a decreases in NO_x 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_x [21,22].

To conclude, ammonia can be formed either by hydrolysis of isocyanates or by direct reaction of stored NO_x with H₂, 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 NH₃ 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_x Trap (LNT) with hydrogen. Storage was achieved with ¹⁴NO and regeneration in the presence of ¹⁵NO [14].

2.2 Ammonia reactivity

As presented above, two primary competing routes are proposed to produce N₂ when H₂ is the reducer: (i) the direct route, from the reduction of stored NO_x by H₂ (Eq. 1), (ii) the sequential route (Eq. 13-14) through NH₃ intermediate formation [24,25]:

This two-steps mechanism was evidenced in Refs. [26] and [20] over a model Pt-Ba/Al₂O₃ catalyst. When the amount of introduced hydrogen is too low to reduce all the stored NO_x, 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. Besides, the reaction of the stored NO_x with hydrogen results in the formation of negligible amount of N₂O and NH₃, nitrogen being the only product detected at the reactor exit. From other works [1,9], no ammonia emission over Pt-Ba/Al₂O₃ 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_x reduction selectivity strongly depends on the hydrogen conversion during the rich pulses [1]. The increase in H₂ concentration in the rich period leads to dramatically change in the N₂/NH₃ distribution at the reactor outlet.

Fig. 1. Pt/Ba/Al₂O₃ catalyst : NO_x conversion at 400°C under cycling lean (60s, 500ppm NO, 10% O₂, 10% H₂O, 10% CO₂) / rich (3s, H₂, 10% H₂O, 10% CO₂) condition. NO_x conversion (%) into N₂ (■) and into NH₃ (■) and related data. Influence of H₂ 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_x-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 ₂ inlet	2000 ppm	8000 ppm	0.85 %	2000 ppm	1.5 %	1500 ppm	3.3 %	2000 ppm	4000 ppm	3.4 %
H ₂ 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 ₃ 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/Al₂O₃ catalyst with Pt-K/Al₂O₃ sample (with similar molar amount of basic element, *i.e.* Ba or K) evidences a higher N₂ selectivity during the reduction step with H₂ of stored NO_x over the K phase [10]. Authors report a similar reactivity for the H₂ + nitrate and NH₃ + nitrate reactions. In fact, on Pt-K/Al₂O₃, the onset for the direct H₂ + nitrate reaction leading to ammonia (step 1, Eq. 13) occurs at temperatures very close to the threshold for the NH₃ + nitrate reaction (step 2, Eq. 14), leading to the desired N₂ compound. It is then proposed that nitrogen formation occurs via a two step pathway. In agreement with Nova *et al.* [28], the stored NO_x react preferentially with the introduced hydrogen to form NH₃ (step 1), whenever H₂ is present in the gas phase. NH₃ further reacts with stored NO_x downstream to form N₂, only in a hydrogen free environment (step 2) [2,20]. The selectivity towards NH₃ formation is governed by the relative constant rates of NH₃ formation and NH₃ consumption. In this dual-step mechanism, step 1 is much faster than step 2 [10,29], even though the characteristic reaction times for NH₃ formation and consumption are lower than the characteristic diffusion times of stored NO_x. 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 H₂ and stored NO_x to nitrogen-containing products (including N₂O, N₂, and NH₃) [24].

This scheme comprises four pathways to N₂O, NH₃ and N₂ formation occurring during the reduction of the stored NO_x by H₂. Especially, it is reported that possible mechanism includes

the activation of H₂ on Pt sites, as reported above. Then, nitrates adsorbed species are decomposed to NO_x and released in the gas phase, due to hydrogen spill-over from the noble metal to the alumina support. NO_x 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 NH₃ yield is significantly decreased over ceria-zirconia mixed oxides (Pt/Ce_xZr_{1-x}O₂), with a beneficial influence of the cerium content. With the increase in H₂ 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/Al₂O₃ model material (Pt/Ba(Mn)/Al catalyst) favours the NO_x 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/Al₂O₃ catalyst is also reported [2]. A synergetic effect is highlighted between Mn and Ce when they are simultaneously added in Pt/BaO/Al₂O₃. 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_x + NH₃ 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 NH₃ emission [31].

Finally, significant ammonia emission is possible at the NSR catalyst outlet. Two pathways are described, the direct route with H₂ 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. NH₃ storage and mechanism in NO_x 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 NH₃-SCR reactions and active sites of metal-exchanged zeolite catalysts is exposed.

3.1 NH₃ reactivity

Among the processes proposed to reduce NO_x species in excess of O₂, a key after-treatment technology is the on-stream reduction of NO_x into N₂ and H₂O over zeolite-based catalysts, using a NH₃ as reducer [32]. The reaction pathway of the NO_x selective catalytic reduction with ammonia (NH₃-SCR) is described by the following reactions (Eq 15-18):

These reactions are usually denoted as “standard” (Eq. 15), “fast” (Eq. 16), “NO₂-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_x with NH₃ 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 N₂ formation requires one nitrogen atom from a molecule of NO_x, 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 NO₂, 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 NO₂/NO ratio is a key parameter for the SCR activity [34,49,50,51,52]. Indeed, fast SCR (Eq. 16) and NO₂-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 NO₂ [54]. In fact, the formation of intermediate Feⁿ⁺-NO species (n = 2, 3), Fe²⁺(NO)₂ complexes, and NO⁺ are reported [55]. Nitrosyl ion (NO⁺) may be produced by N₂O₄ disproportionation, which is firstly formed by NO₂ dimerization. NO⁺ can further react with H₂O to produce HNO₂. HNO₂ can then react with ammonia to produce ammonium nitrite (NH₄NO₂), which decomposes quickly below 100°C, leading to the SCR products, N₂ and H₂O [56]. Ammonium nitrate can also be formed (Eqs. 19-20):

In this later process, NH₃ is activated on zeolitic Brønsted acid sites, giving NH₄⁺ ions [57]. This point is discussed below (section 3.2). Ammonium nitrate thereafter decomposes into NO₂ and NH₃, 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 NH₃-SCR, N₂O emission can be also observed. N₂O emission however constitutes the main drawback of this system. For instance, Wilken *et al.* [59] reports a maximum N₂O production at 200°C over

Cu-Beta zeolite. Mechanism of N₂O emission is proposed to proceed through the decomposition of ammonium nitrates (Eq. 22):

Fast SCR conditions, and more especially high NO₂ concentrations, are also proposed to favor the N₂O 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 NH₃-SCR mechanism, ammonia is firstly adsorbed and activated as NH₄⁺ 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_x 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 NH₃-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 [NH₄⁺_x][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-NH₄⁺ compound (NH₄⁺ bonded to three hydrogen atoms) in small pore size support [65]. 3H-NH₄⁺ compound is also reported as necessary for the formation of the active [NH₄⁺_x][NO] complex during the NH₃-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 NH₃-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 NO₂ 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 NH₃ 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 NH₃-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⁻¹ [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_x.

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]²⁺ dimer species are proposed to catalyze NH₃-SCR reaction at low temperature ($T \leq 300^\circ\text{C}$) [73]. To the opposite, Cu²⁺ 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_xO_y clusters like Fe₄O₄, isolated Fe²⁺ and Fe³⁺

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 ≈ 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 NH_3 oxidation [81].

Other catalytic systems are also studied for the abatement of 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 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 NO to NO_2 . Coordinated ammonia would be oxidized to amide species, which later reacts with 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 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 NO_x conversion into N_2 , and the significant production of N_2O . 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 V_2O_5 occurs from 650°C [85,86]. Then, new catalytic systems, having high efficiency at low temperature, thermally stable up to 800°C and with a limited impact of the NO_2/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 NO_x were reduced to N_2 at only 200°C [88]. The promotion of acidic zirconia by ceria also increases the NO_x conversion, the selectivity to 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 NO_x SCR by NH_3 , are the more quoted materials for a coupling with a NSR catalyst.

4. Coupling of NO_x trap and NH_3 -SCR catalysts

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

The concept of adding a NH_3 adsorbing materials to a 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, NO_x can be reduced to N_2 and NH_3 which can be stored on the zeolitic materials. When the engine turns to lean conditions, NO_x is no longer reduced on the TW catalyst. Ammonia is in part oxidized (to 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 NO_x issued from the main engine [90]. Exhaust pipes are arranged to receive a TWC catalyst and a 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 NH_3 adsorbing and oxidizing catalysts (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 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 NO_x -trap materials (named NO_x -occluding and reducing catalyst, NH_3 -OR in the patent) [92]. In this configuration, the system is very close to the NSR-SCR coupling for 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 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 NO_x with reducers in excess (especially 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 NO_x adsorbing catalyst. Commercially, the system was implemented on the Mercedes E320 Bluetec vehicle in 2007.

The coupling between a NO_x -trap sample and a 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 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 NO_x not stored on the NSR catalyst. The Ford patent claims a NSR catalyst composed of

noble metals deposited on a NO_x-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 Ag₂WO₄ 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_x-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/Al₂O₃ 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-Al₂O₃, NSR (Pt-Rh/BaO/Al₂O₃) 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_x 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 NO₂.

The effect of Cu-ZSM-5 (5%Cu) addition on the performances of Pt-Rh/BaO/Al₂O₃ (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_x 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 H₂ in the reductant mixture. This is in line with H₂ 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 NH₃-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% H₂O in the gas mixture did not cause great difference in NO_x 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/H₂ + 167 ppm C₃H₆ + 1% CO₂ + 10% O₂ in He) and 10 s rich (100 ppm NO + 8.53% CO/H₂ + 1% CO₂ in He). The gas mixture CO/H₂ contains 75% CO and 25% H₂. Entry 2; results with pure CO.

Entry	Catalyst	NO _x removal		
		250°C	300°C	400°C
1. With H ₂	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 ₂	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+H₂+C₃H₆ mixture as the reductant in cycling experiments, NO_x 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_x 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/Al₂O₃ 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/Al₂O₃ and Fe-ZSM-5). As expected, NO_x 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_x slipped from during the lean phase reacts with NH₃ stored on Fe-ZSM-5 to give N₂. 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 CO₂ and H₂O 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_x removal, in the presence and in the absence of CO₂ 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_x removal, it leads to a higher selectivity to N₂ in rich phase, when there is no CO₂ and H₂O and in both phases (lean and rich) in the presence of CO₂ and H₂O.

The results of Tables C and D were obtained at 250°C. In the physical mixture, the amount of removed NO_x decreases with the temperature in absence of CO₂ and H₂O while it is almost constant with CO₂ and H₂O. At 350°C, there is virtually no difference when there is CO₂+H₂O or not in the gases. In the dual bed, the amount of removed NO_x tends to increase with temperature in every cases (with CO₂+H₂O 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 CO₂ and H₂O. Experimental conditions: T = 250°C; lean phase NO (1000 ppm) in O₂ (3% v/v) + He; rich phase H₂ (2000 ppm) in He; catalyst weight 60 mg LNT (or 60 mg NSR + 60 mg SCR); total flow rate 100 Ncm³/min mol/gcat refers to NSR Pt–Ba/Al₂O₃ weight. From ref. [111].

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

Table D: Same results with 0.1 % CO₂ and 1% H₂O 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 _x removed (a)	272	323	396
NO _x stored(a)	272	307	272
N ₂ (lean)	0	16	123
N ₂ (rich)	93	21	135
NH ₃ 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_x 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_x removal efficiency and percentage of ammonia used to reduce NO_x in a smart catalytic converter based on Pt-Ba-NSR and Fe-zeolite SCR catalyst. Reaction conditions: 240°C, 165s lean (500ppm NO + 8%O₂ + 8%CO₂ + 8%H₂O), 7s rich (500ppm NO + 1.6%O₂ + 1.4%H₂ + 0.3%C₃H₆ + 4.2%CO + 11.5%CO₂ + 8%H₂O). From ref. [112].

Catalyst configuration. Respective volumes	% NO _x removed on the NSR unit	% NO _x removed on the SCR unit	NH ₃ reacted/ NH ₃ 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 N₂O. In the NSR-SCR coupling, it is important to minimize (or annihilate) both ammonia and N₂O in the aftertreatment exhaust gas. This means that ammonia should be used to reduce NO_x (or be oxidized to N₂) while N₂O, if formed, should be destroyed in the catalytic system. The NSR catalyst was composed of Pt/Pd/Rh/Ba/Ce/Zr on Al₂O₃ (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_x abatement, the system with an equal volume of NSR and SCR catalysts shows the best result in terms of ammonia and N₂O slip. A similar configuration was adopted by Pereda-Ayo to study the NSR (Pt-Ba-Al₂O₃)-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 H₂

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/Al₂O₃+ 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 NH₃-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/Al₂O₃) is active in NO_x reduction by hydrocarbons or alcohols but it produces also ammonia and HCN which is used in the second bed (CuCoY or Pd/Al₂O₃) to reduce the unconverted NO_x by ammonia.

5. Conclusion and perspective

The combination of NO_x trapping materials with NH₃-SCR catalysts for the NO_x treatment from mobile lean-burn engines has been investigated. Particular attention has been paid in mechanism of ammonia emission and reactivity towards NO_x 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_x. 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_x reduction mechanism, by a sequential route in which NH₃ reacts faster with NO_x to yield N₂ 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 NH₃ yield.

Ammonia may likewise be used as reducer for selective catalytic reduction of NO_x species. For this application, metal-exchanged zeolite catalysts offer new opportunities to reduce NO_x emissions from lean-burn engine via the NH₃-SCR process. Iron-exchanged ZSM-5 has received much attention because of its promising activity and stability in the NH₃-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 ≈ 1) seems to be proscribed creating extra-framework metal oxide clusters, which can be highly active for NH_3 oxidation.

The coupling between a NO_x -trap catalyst and a NH_3 -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_x conversion can be achieved, depending on the working conditions. Whatever the zeolite used, higher performances are reported with H_2 as reducers, since it enhances NH_3 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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