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Fabien Can, Xavier Courtois, Daniel Duprez. NSR–SCR Combined Systems: Production and Use of Ammonia. I. Nova and E. Tronconi Eds. Urea-SCR technology for DeNO_x after treatment of Diesel exhausts, Springer, pp.587-622, 2014, Fundamental and Applied Catalysis series, 10.1007/978-1-4899-8071-7_19 . hal-03109298

HAL Id: hal-03109298

<https://hal.science/hal-03109298>

Submitted on 13 Jan 2021

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“Urea-SCR technology for DeNO_x after treatment of Diesel exhausts”.
I. Nova and E. Tronconi Eds (Springer, Fundamental and Applied Catalysis series)
Chapter 19, p. 587-622 (2014).
DOI: 10.1007/978-1-4899-8071-7_19

NSR-SCR combined systems: production and use of ammonia.

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Abstract

This chapter 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 (NO_x + H₂) 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.

1. Introduction

Beside the NH_3 /urea SCR process, the NO_x reduction from lean burn exhaust gas can be achieved using the cycled NO_x -Storage Reduction or NSR system (also called Lean NO_x -trap (LNT) system). In Europe, the NH_3 -SCR technology could be quickly implemented on heavier cars, as it is already the case for trucks, while the NSR system is rather envisaged to be implemented in light passenger car.

However, 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. Ammonia emission is proscribed but this undesirable product is also a very efficient NO_x reductant, available in the exhaust gas. Then, logically, the addition of a NH_3 -SCR catalyst to the NSR catalyst was proposed in order to increase the global NO_x abatement and the N_2 selectivity. Ammonia is produced during the brief regeneration period of the NSR catalyst, and it has to be firstly stored on the SCR catalytic bed. During the next lean period, this stored NH_3 can react with NO_x passing through the NO_x -trap, via the NH_3 -SCR reaction.

Then, the addition of a NH_3 -SCR material to the NSR catalyst is a possible way to increase the global NO_x abatement and maximize the N_2 selectivity, together with the prevention of the ammonia slip. A schematic view of the process is presented in Figure 1.

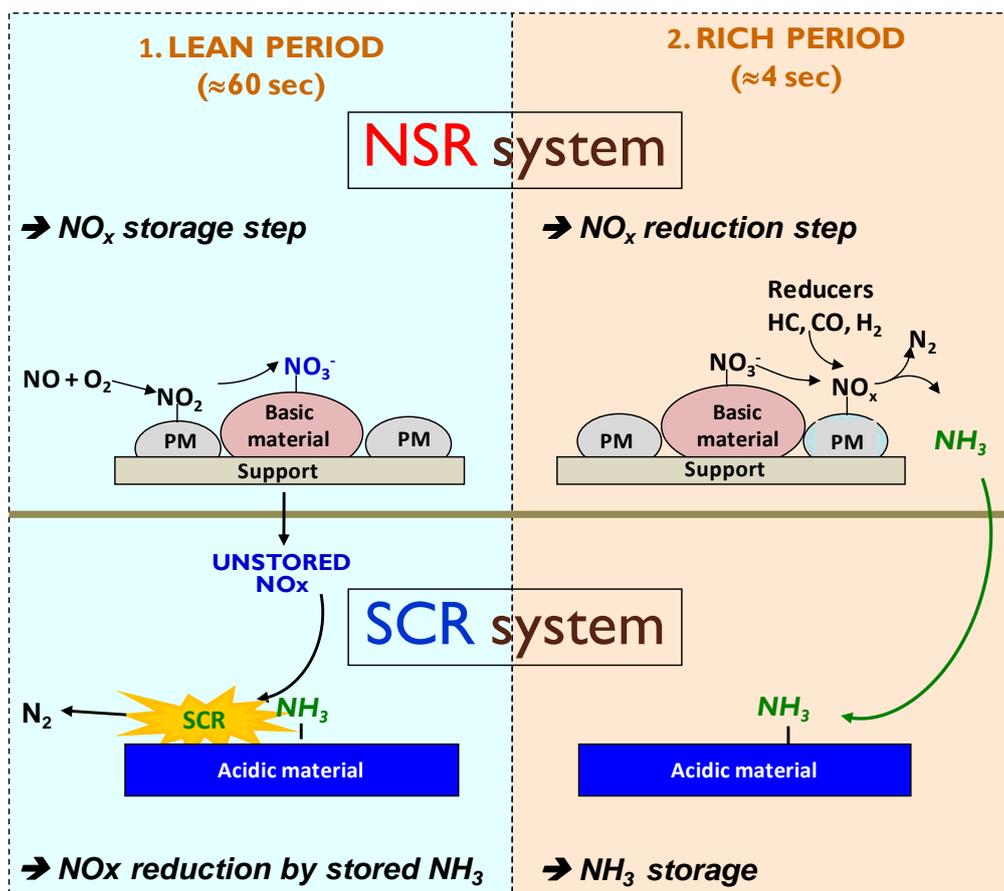


Figure 1: schematic view of the NSR+SCR combined process.

This work reports firstly recent results about the production of ammonia during the NSR process, and then an overview of the recent advances in NOx abatement in excess of oxygen using the NOx storage-reduction (NSR) - Selective Catalytic Reduction (SCR) combined systems. With this aim, zeolites are the main studied SCR materials. In addition, studies about the NH₃ storage and the mechanism in NOx reduction over zeolite are presented.

2. NH₃ emission from NSR catalysts

2.1 The NSR process

The NOx storage-reduction (NSR) process is largely studied since the beginning of the 1990s [1-5]. Model NOx-trap catalysts usually contain a noble metal (Pt) allowing the NO oxidation into NO₂, and a basic phase (Ba oxide/carbonate) in order to trap NO₂ as nitrite/nitrate intermediates. Both precious metals and storage phase are usually supported on a modified

alumina support [6]. Other frequent components are rhodium which is known to favor the NO_x reduction into N₂ in stoichiometric/rich media, and cerium based oxides due to their redox behavior, the NO_x storage capacity and the sulfur resistance [7,8]. Among other possible basic storage phases, potassium is the more frequently proposed [9,10].

The NSR catalyst operates in fast lean/rich transients. During the lean steps of approximately one minute, the gas phase is constituted by the standard exhaust gas from the lean burn engine. NO is then oxidized into NO₂ over the precious metals and further trapped as nitrite/nitrate on the basic components of the catalyst. The "saturated" trap is then regenerated during short incursions in rich media for few seconds in order to reduce the stored NO_x into N₂. In fact, the rich phases are generated by injecting pulses of fuel, immediately transformed into HC, CO and H₂ on a pre-catalyst (usually a Diesel Oxidation Catalyst implemented before the NSR system). These rich pulses induce exothermic reactions which favor the nitrate desorption and reduction into nitrogen. These steps correspond to the ideal operating mode of the NSR system.

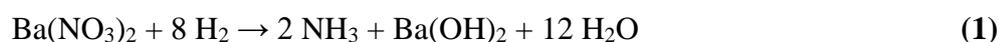
The nature of the reductants in the rich mixture directly impacts the NO_x conversion and the selectivity of the NSR reaction. On usual NSR model catalysts, namely Pt/(BaO)/Al₂O₃, hydrogen is reported to be the more efficient agent compared with CO or propene [11-13]. This higher efficiency of H₂ was evidenced by Szailer *et al.* [11] at very low temperature (150°C), and in the 150-350°C temperature range by Nova *et al.* [12]. Nevertheless, undesirable by-products can also be emitted during the regeneration, such as N₂O and ammonia. As an introduction to the NSR+SCR combined system, the following section focuses on the ammonia formation and emission over NSR catalysts.

2.2 Ammonia formation pathways

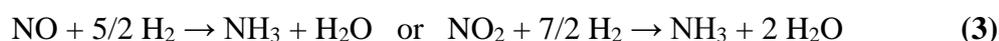
Ammonia is reported to be produced only during the rich phases of the NSR process, even in the presence of usual reductant(s) such as H₂, CO or propene during the lean phases [14,15].

However, note that significant ammonia emission can be observed during the NO_x reduction in lean condition using ethanol as reductant [16].

During the regeneration of the NO_x trap, two major routes are commonly admitted for the ammonia formation. The first one is the direct reaction of stored NO_x with hydrogen, as described in reaction (1) [17,13]. This route was proposed over Pt-Ba/Al₂O₃ material, when H₂ is used as the reductant [18]. Artioli *et al.* [19] observed that, depending on the gas feed composition, ammonia is emitted together with CO₂ consumption, as reported in reaction (2).

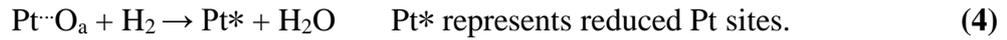


The catalyst temperature is an important parameter which impacts both the NO_x adsorption/desorption equilibrium and reduction rate. Ideally, the NO_x reduction rate has to be higher than the NO_x desorption rate in order to limit the NO_x slip during the rich pulses. During these reduction phases, a part of the introduced reductants also reacts with remaining oxygen from the gas phase or stored on the catalyst. As a consequence, an exothermic phenomenon is generally detected during the rich pulses, which lead to additional releases of unreduced NO_x. In fact, it was showed that when the regeneration of the catalyst is carried out in the presence of NO in the feed stream, ammonia can be directly formed according reaction (3) in the reactor zone where the trap is already regenerated [20].

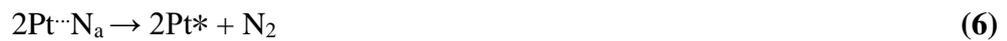
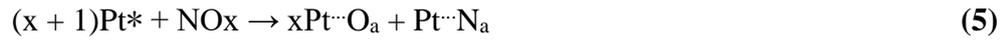


However, it is shown in this work that ammonia is observed after N₂ formation, when hydrogen begins to be emitted. This point is more detailed in section 2.3.

The direct ammonia formation mechanism (reactions 1 and 3), when only H₂ is used as reductant, was studied in Ref. [11]. Authors proposed that hydrogen reacts firstly with the platinum surface on which oxygen species (O_a), resulting from the reduction of NO₂, remain adsorbed (reaction 4).



The produced H₂O is supposed to destabilize the adsorbed nitrates which are suggested to be decomposed on the free Pt surface. The dissociation of NO_x species on platinum can thereafter leads to the recombination of N_a atoms to form N₂ (reactions 5 and 6), or to the reaction of these N_a atoms with H₂ to form NH_x and, finally, NH₃.

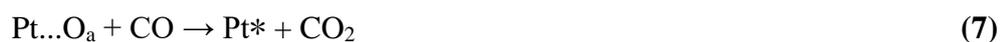


In this step way, the initial role of H₂ is the reduction of the platinum surface to allow the NO_x dissociative adsorption [21].

Clayton *et al* [22] also suggested that the ammonia formation mechanism includes the activation of H₂ on Pt sites. They proposed that adsorbed nitrates are decomposed into 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 local H/N ratio.

The second way to obtain ammonia during the NSR regeneration is the “isocyanate route” [23]. This intermediate reaction is observed when a carbon source is present in the reaction mixture, especially CO [11]. However, CO can also be produced in situ, for instance by the reverse water gas shift (RWGS) reaction between H₂ and CO₂, the later being always present in large amounts in a real exhaust gas (see also the influence of the WGS equilibrium section 2.3).

At low temperature (T < 150°C), the first reaction is still the removal of adsorbed oxygen atoms from the Pt particles (Pt^{...}O_a), leading to CO₂ production (reaction 7).



The obtained free Pt sites become available for the NO_x dissociative adsorption and the CO adsorption. Then, formation of adsorbed NCO species is possible according reaction 8.



-NCO species generated on the Pt particles migrate to the oxide components of the catalyst,

usually alumina. Therefore, -NCO and CO₂ formation occur at the expense of the reduction of the adsorbed NO_x, while N₂ is not produced.

At higher temperatures (T > 300°C), these -NCO species are able to react with the stored NO_x. This reaction route eventually leads to the consumption of both nitrate and NCO adsorbed species according reaction 9.



In real exhaust gas, water is present with a large extend and it is reported that N₂ formation is significantly enhanced by adding water to the NCO-covered catalysts [10]. Adding water leads to a new reaction route for the -NCO reactivity, i.e. the hydrolysis of -NCO species to NH₃ and CO₂ (reactions 10 and 11).



To conclude, ammonia can be formed only during the regeneration steps of the NO_x-trap, even if ammonia release can also occur during the subsequent lean phase. Two pathways are described: the direct reaction of H₂ with the stored NO_x or with NO_x present in the gas phase, and via the hydrolysis of isocyanates species. Hydrogen is reported as a more efficient reductant than CO, leading to a higher emission of ammonia [11,12].

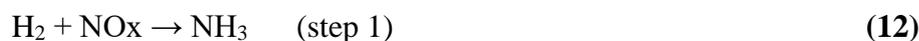
2.3 Influencing parameters/ammonia reactivity

Numerous parameters were studied and reported as influencing the ammonia emissions from the NSR catalyst.

Dispersions of the catalyst components were reported to strongly modify the NH₃ emission, For instance, Castoldi *et al.* have observed that ammonia emission occurs during the NO_x-trap regeneration when barium loading ranges from 16 to 30 wt.% [18]. 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.

Bhatia *et al.* [24] have modeled the effect of the platinum dispersion of a model Pt/BaO/Al₂O₃ sample, also taking into account the influence of the temperature. This study indicates that at high temperature ($T \geq 300^{\circ}\text{C}$), highest amounts of NH₃ are produced over low dispersed catalyst (3.2% platinum dispersion). On the contrary, it was observed that ammonia formation is enhanced at low temperature ($T \leq 200^{\circ}\text{C}$) with the highly dispersed catalyst (50% dispersion) [24]. The effect of noble metal dispersion on ammonia production is explained by the variation of the average distance – or proximity – between the stored NO_x and the platinum sites. Proximity between storage sites and reaction sites is known to affect the stored NO_x transport process [25].

As presented in section 2.2 above, two main routes are proposed to produce N₂ when H₂ is the reductant: (i) the direct route, from the reduction of stored NO_x by H₂, and (ii) the sequential route through NH₃ intermediate formation [22,26], which can be simply described following reactions (12-13).



This two-steps mechanism was evidenced in Refs. [27] and [34] over a model Pt-Ba/Al₂O₃ catalyst. As a consequence, 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. Beside, the reaction of the stored NO_x with hydrogen results in the formation of negligible amounts of N₂O and NH₃, nitrogen being the only product detected at the reactor exit. It induces that no ammonia is observed as long as hydrogen is fully consumed. It is especially true for temperature higher than 300°C, as confirmed by different works [12,28,29]. In opposition, the NO_x reduction selectivity is strongly affected by ammonia emission since hydrogen is not fully converted during the pulses. In Table 1 are reported some results from

literature in which the hydrogen concentration measurement at the reactor outlet is available.

Table 1 shows that, whatever the NO_x conversion rate, ammonia is released when hydrogen is not fully consumed during the regeneration step of the NO_x-trap catalyst.

Table 1: Examples of data from the literature about the correlation between the ammonia emission and the presence of unconverted hydrogen during storage/reduction cycled experiments.

Ref	Lietti <i>et al.</i> [32]	Pereda-Ayo <i>et al.</i> [27]	Castoldi <i>et al.</i> [18]	Bhatia <i>et al.</i> [24]	Kočí <i>et al.</i> [13]	Nova <i>et al.</i> [12]	Artioli <i>et al.</i> [19]	Choi <i>et al.</i> [30]
Catalyst	Pt-Ba/Al	Pt-Ba/Al monolith	Pt-Ba/Al	Pt-Ba/Al	Industrial	Pt-Ba/Al	Pt-Ba/Al	Industrial
T (°C)	100	260	350	370	250	200	350	200
H ₂ inlet	2000ppm	0.85%	2000ppm	1500ppm	3.3%	2000ppm	4000ppm	3.4 %
H ₂ outlet	80ppm	Traces	600-150ppm	700ppm	0.5%	300ppm	1000ppm	1.4 %
NH ₃ outlet	400ppm	300ppm	150-400ppm	330ppm	2200ppm	180ppm	500ppm	120ppm

An illustration of these observations is given Figure 2. This figure reports the influence of the catalytic mass and the hydrogen concentration in the rich pulses at 400°C. It allows following the evolution of the reactions along the catalytic bed. The increase of the catalytic weight clearly shows that the *in situ* produced ammonia during the NO_x reduction on the first part of the catalyst is able to react with the downstream stored NO_x to give N₂ since there is no more available hydrogen [28]. On the contrary, if hydrogen remains, all the catalytic bed works identically.

In agreement with Nova *et al.* [31], this Figure 2 also strongly suggests that (i) nitrogen formation occurs via a two step pathway, and (ii) 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, preferentially in a hydrogen free environment (step 2) [28,34]. The selectivity towards NH₃ formation is then governed by the relative constant rates of NH₃ formation and NH₃ consumption. In this dual-step mechanism, step 1 rate is higher than the step 2 one [17,32], even though the characteristic reaction times for NH₃ formation and consumption are lower than the characteristic diffusion times of stored NO_x.

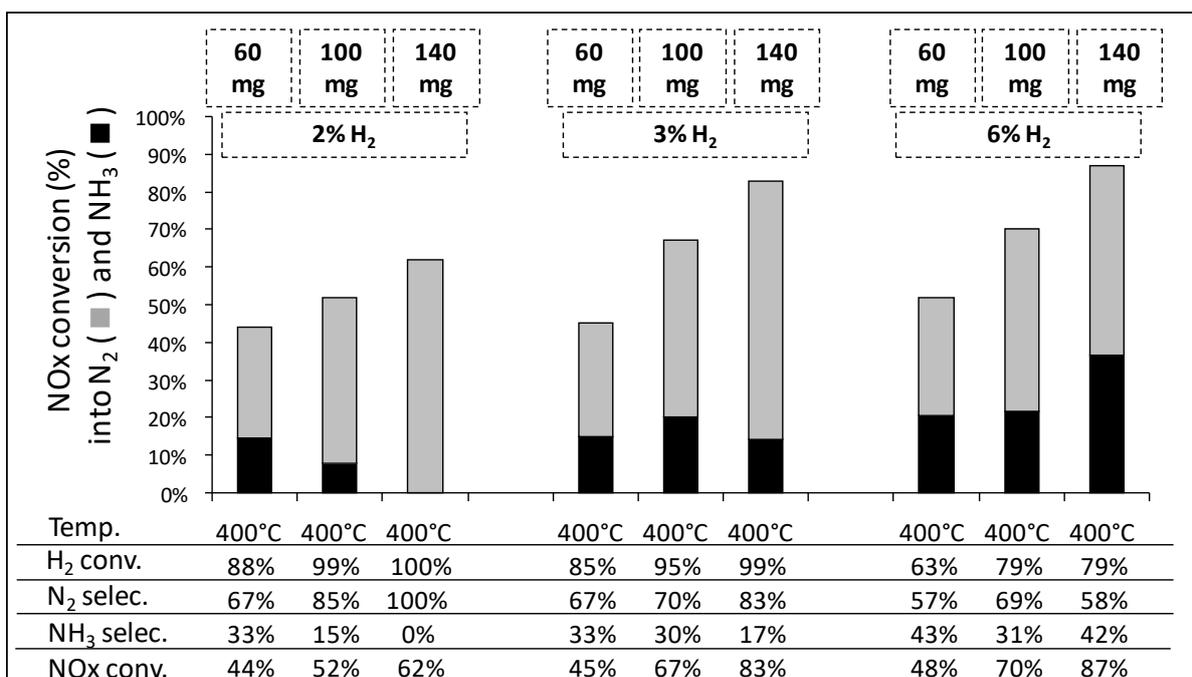


Figure 2: Pt/Ba/Al₂O₃ catalyst: NO_x conversion at 400°C under cycling lean (60s, 500ppm NO, 10% O₂, 10% H₂O, 10% CO₂) / rich (3s, H₂, 10% H₂O, 10% CO₂) condition. NO_x conversion (%) into N₂ (■) and into NH₃ (■) and related data. Influence of both the H₂ concentration in the rich pulses (1–6%) and the catalyst mass (60, 100 and 140 mg), from [28].

As previously mentioned, the presence of H₂O and CO₂ in the gas mixture directly impacts ammonia formation mechanism. According to reaction (14), 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 reductant in the rich mixture is H₂ or CO alone.



It was demonstrated that the presence of water or carbon dioxide in the gas mixture has a negative effect on the storage step of the NSR process [33,34]. However, their impacts on the reduction step using H₂ as reductant are significantly different. Due to the involvement of water in the (R)WGS reaction, the absence of few percents H₂O in the gas mixture leads to a small decrease of the NO_x removal efficiency because a larger part of the introduced hydrogen is transformed into CO, a less efficient reductant. In the same time, the ammonia selectivity increases due to the possible formation of isocyanate species. In opposition, the absence of CO₂ leads to an increase in NO_x conversion [34], with a little ammonia formation. The isocyanate is then impossible since there is no carbon source in the gas mixture. However,

ammonia emission can still be observed, indicating that the direct route occurs. Note that hydrocarbons (such as propene) are also possible reductants leading to isocyanates via oximes intermediates [35]. Isocyanates lead to amines (or amides) that are very good reductants of NO_x [35,36].

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 for the NO_x stored over the K phase [17]. 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, reaction 13) occurs at temperature very close to the threshold for the NH₃ + nitrate reaction (step 2, reaction. 14), leading to the desired N₂ compound. Finally, this study show again that the ammonia emission strongly depends on the balance between the ammonia production and the ammonia reaction with the stored NO_x.

The nature of the support, especially in terms of redox properties, obviously significantly impacts this equilibrium between formation and reactivity of NH₃ during the regeneration step of the NSR process. It is possible to increase the reaction rate between the *in situ* produced ammonia and the remaining stored NO_x. For instance, addition of manganese to a Pt/BaO/Al₂O₃ model material (Pt/Ba(Mn)/Al catalyst) allows an improvement of the NO_x reduction by ammonia, especially at 400°C, even if the introduced hydrogen is not fully converted [28]. Same trends were obtained with addition of ceria, and more interestingly, further improvements were obtained with the simultaneous Mn and Ce addition to model Pt/BaO/Al₂O₃ catalyst [29]. A synergetic effect was highlighted between Mn and Ce with a significant decrease in ammonia emission in the 200-400°C temperature range, correlated with a synergetic effect concerning the oxygen storage capacity. The influence of the Mn and

Ce addition on the NO_x conversion rate and the NH₃ selectivity at 400°C are presented in Figure 3 depending on hydrogen concentration in the rich pulses. The increase of the NO_x conversion together with the decrease of the ammonia selectivity was partially attributed to an enhancement of the reactivity between the *in situ* produced ammonia and the stored NO_x.

In addition to the enhancement of the NO_x + NH₃ reaction rate, the selective ammonia oxidation into nitrogen via the available oxygen was also proposed to occur [22]. Then, this reaction was proposed to explain the low NH₃ emission obtained with the catalysts exhibiting high oxygen storage capacities (OSC), even with very large hydrogen excess (Figure 3, [37]). However, the OSC/oxygen mobility is not the only parameter to explain the activity enhancement. It was showed over Pt/Ce_xZr_{1-x}O₂ catalysts that the NH₃ yield is decreased with the increase of the cerium content, but not with the OSC [38]. This aspect is not totally explained yet.

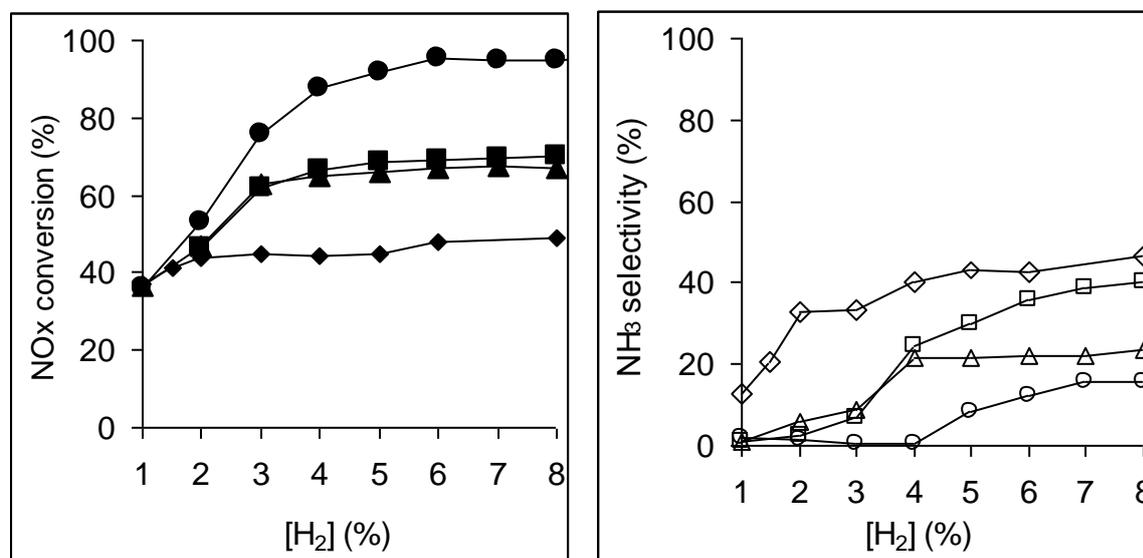


Figure 3: NO_x conversion rate (full symbols) and NH₃ selectivity (open symbols) measured at 400°C depending on hydrogen concentration in the rich pulses for Pt/20Ba/Al (◆,◇), Pt/20BaMn/Al (■,□), Pt/20BaCe1/Al (▲,△) and Pt/20BaMnCe0.5/Al (●,○) [29].

2.4 Conclusion

Finally, significant ammonia emissions are 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. Whatever the ammonia production pathway, ammonia emission strongly depends on the balance between the ammonia formation rate and the ammonia reactivity (with NO_x or oxygen from the support). Ammonia emission is particularly linked to the presence of unconsumed hydrogen. In addition, Ce-based oxides are proved to enhance the ammonia reactivity in the NSR catalyst.

3. Coupling of NO_x trap and NH₃-SCR catalysts

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

The concept of adding a NH₃ adsorbing materials to a NO_x reduction catalyst was patented by Toyota in 1998 for applications on gasoline engines [39]. 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 N₂ and NH₃ 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 N₂) 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 [40]. Exhaust pipes are arranged to receive a TWC catalyst and a NH₃ 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 [41]. TW catalysts and NH₃ adsorbing and oxidizing catalysts (NH₃-AO) are interconnected to receive alternatively the gases issued from the first and second groups of cylinders. The patent claims a wide range of NH₃-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, NH₃-OR in the patent) [42]. 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 [43,44].

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" [45]. 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 reductants in excess (especially H₂) during the rich operating phases. The materials catalyzing the reaction between NO and ammonia are 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 NH₃-SCR catalyst, located downstream the first one or in a double layer on the monolith, was patented by Ford in 2004 [46]. 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 [47]. Chigapov *et al.* from Ford Germany recently published a patent in which special compositions of the LNT catalyst (based on rare-earth and earth alkaline oxides) and of the SCR catalyst (Cu-Ce zeolites) were claimed for a

better use in LNT-SCR coupling [48]. The coupling between a NSR and a SCR catalyst was also claimed by Engelhardt [49]. 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 [50]. In this patent, the claimed SCR catalyst is composed of silver tungstate Ag_2WO_4 supported on alumina. Other BASF patents were published in 2010 and 2011 to cover the specific case of NSR-SCR coupling systems [51,52]. A NSR-SCR coupling system was also depicted by Johnsson-Matthey [53]. Indeed, recently Twigg *et al.* suggest the development of a multi component diesel catalyst known as “four-way catalysts” (FWCs) [54]. 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. Finally, in the last 10 years, great efforts were made at Eaton Corporation to propose a viable technology with different configurations. No less than 6 patents were published by this Company claiming both depollution systems and catalysts for each configuration [55-60]. The systems may include two LNT bricks in parallel with optimization (i) of thermal changes during working and desulfation and (ii) of rhodium usage in the LNT catalyst.

3.2 Coupling of Pt catalysts with zeolites

Addition of non-promoted zeolites to a NSR catalyst was investigated by Nakasutji *et al.* in 2007 [61]. They showed that mordenites with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 10 or 20 were able to store significant amount of ammonia during the NO_x-trap/reduction process and to improve NO_x conversion. Preliminary experiments were carried out in a rich gas (400 ppm NO+1% H_2) and in simplified lean/rich cycles (lean: 2000ppm NO + 8% O_2 ; rich: 2% H_2). They revealed that Pt/ Al_2O_3 (without Ba) was able to produce ammonia during the rich phase (NO/ H_2 mixture) and that MOR-10 or 20 could store ammonia in similar conditions. In spite of these reactive and adsorptive properties, the physical mixture composed of 20 parts Pt/ Al_2O_3 and 80 parts of MOR-20 is much less efficient for NO_x conversion than a standard

NSR catalyst (Table 2). This is due to the very poor NO_x-trap properties of the Pt-Al₂O₃: as there is no NO_x trapped on the Pt catalyst, no ammonia could be produced during the rich phase. By contrast, the conversion is much higher when Pt/Al₂O₃ is replaced by Pt/CeO₂ which possesses significant NO_x-trap capacity. Ammonia stored on the mordenite contributes for 50%, 45% and 30% of NO_x conversion at 200°C, 300°C and 400°C respectively. Unfortunately, relatively large amounts of N₂O are produced at 200-300°C, which limits the conversion to N₂.

Table 2

Effect of the addition of mordenites to Pt catalysts (2%Pt/Al₂O₃ or 2%Pt/CeO₂) for NO_x conversion in cycled conditions (physical mixture of 80 part of MOR-20 and 20 part of Pt catalyst). Comparison with a NSR catalyst alone (2 wt.% Pt/75% alumina-21 wt.% BaCO₃-2 wt.% K₂CO₃). From ref. [61] Selectivities are not detailed in this reference.

Catalyst	NO _x conversion at various temperatures				
	200°C	250°C	300°C	350°C	400°C
NSR alone	22.0	77.2	94.9	95.3	96.5
Pt/Al ₂ O ₃ + MOR	19.6	28.4	27.1	14.5	5.4
Pt/CeO ₂ + MOR	41.8	75.7	68.6	47.5	32.8
<i>Conv. to N₂</i>	28.6	38.5	49.0	41.8	18.4

3.3. Coupling of Pt(RhPd)/BaO/Al₂O₃ with Cu-zeolite catalysts

The NSR-SCR coupling was studied by Shinjoh *et al.* who used Cu-ZMS5 as the SCR catalyst [62]. A three-bed reactor was developed comprising successively: a 2.4%Pd/γ-Al₂O₃ catalyst (simulating the Diesel Oxidation Catalyst), the NSR catalyst (1.6%Pt-0.16%Rh/BaO/Al₂O₃) and the SCR catalyst (5%Cu-ZMS-5). 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. The increase of conversion can amount to +15% when Cu-ZSM-5 is added (Figure 4).

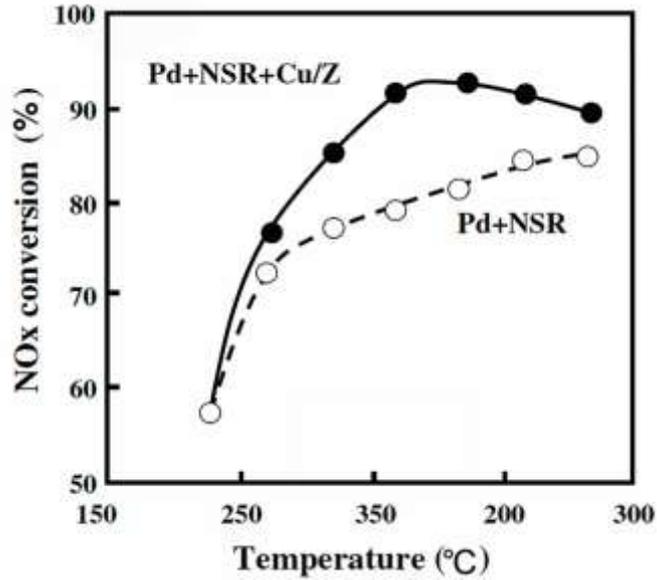


Figure 4: Effect of Cu-ZSM5 added to the Pd+NSR catalyst

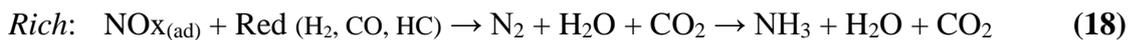
Lean gas: 230 ppm NO, 6.5 vol% O₂, 9.6 vol% CO₂, 3 vol% H₂O balanced N₂,

Rich gas: 230 ppm NO, 0.4 vol% O₂, 3900 ppmC with C₃H₆ as HC, 9.6 vol% CO₂, 3 vol% H₂O balanced N₂

The role of each catalyst was detailed by Shinjoh *et al.* The **Pd catalyst** allows the NO oxidation into NO₂ in the lean phase (reaction 15) and significantly increases the NH₃ formation during the rich phase (reaction 16):



A third role of the Pd catalyst is to catalyze partial oxidation of propylene in reducing conditions, C₃H₆ being then partially transformed into H₂ and CO. The **NSR catalyst** stores the NO_x during the lean phase (reaction 17) and forms N₂ or NH₃ during the rich phase (reaction 18).



Finally the **SCR catalyst** stores ammonia during the rich phase (reaction 20) and allows the reaction of adsorbed ammonia with NO not converted in the lean phase (reaction 19).



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.* [63,64]. 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 3.

Table 3: 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.

Reductant	Catalyst	NOx removal		
		250°C	300°C	400°C
CO/H ₂ mixture	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
Pure CO (6.4%)	Pt-Rh/Ba (NSR alone)	39	43	36
	Pt-Rh/Ba + CuZSM-5 (2 beds)	39	58	42
	Pt-Rh/Ba + CuZSM-5 (phys. mix.)	54	66	45
Pure H ₂ (6.4%)	Pt-Rh/Ba (NSR alone)	47	54	48
	Pt-Rh/Ba + CuZSM-5 (2 beds)	67	73	42
	Pt-Rh/Ba + CuZSM-5 (phys. mix.)	68	77	45
Pure H ₂ (2.14%)	Pt-Rh/Ba + CuZSM-5 (2 beds)	62	60	-
	Pt-Rh/Ba + CuZSM-5 (phys. mix.)	67	61	-

While Cu-ZSM-5 is almost inactive in NOx 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. At 400°C, there is virtually no improvement when Cu-ZSM5 is added to the NSR catalyst. At this temperature, ammonia is either not produced or not stored on the SCR catalyst. 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. The greatest effect of Cu-ZSM-5 is observed in the presence of H₂ in the reductant mixture, independently of the catalyst configuration (physical mixture or two beds). This is in line with H₂ giving the highest yield of ammonia in NSR cycling conditions.

However, a cooperative effect between H₂ and CO can be observed at low temperature on the physical mixture, the reductant efficiency being in the following order: CO/H₂ mixture > H₂ alone > CO alone. 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. Another critical point is the process selectivity: residual NH₃ is a criterion of the NSR-SCR efficiency (ammonia slip cannot be accepted) while N₂O formation is a good criterion of the reduction selectivity (N₂O is a powerful greenhouse effect gas). Figure 5 shows the NH₃ and N₂O concentration after the NSR catalyst and in the NSR-SCR configuration.

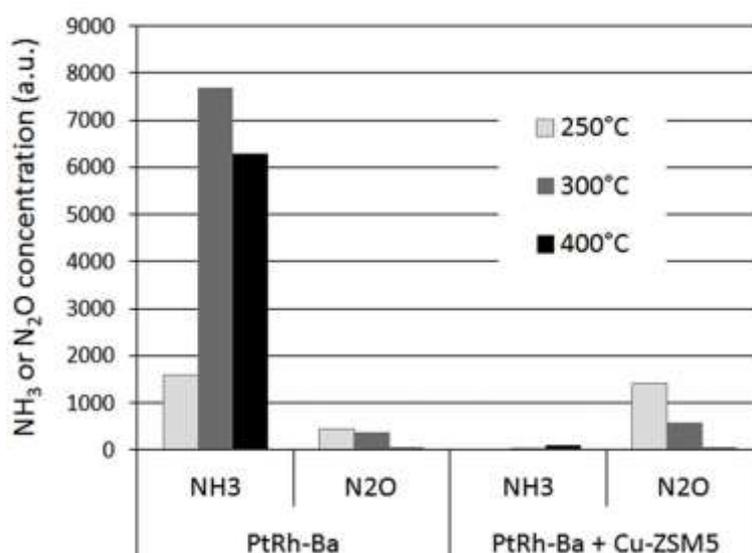


Figure 5: Selectivity to NH₃ and N₂O of the NSR catalyst alone and in the NSR-SCR dual bed configuration. Gas compositions during lean and rich phases are detailed in Table 3.

A similar system (Pt-Rh NSR + Cu-zeolite) was recently investigated by Mc Cabe *et al.* [65-67] of Ford Motor Company. Figure 6 shows the implementation of the catalysts in the exhaust line for the engine tests.

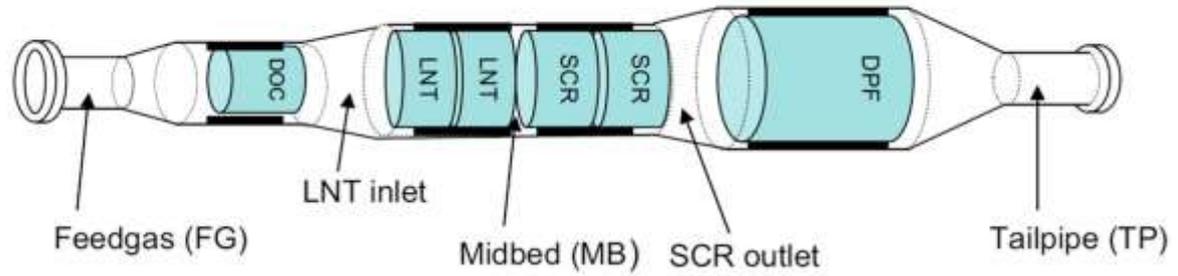


Figure 6: System used in the vehicle tests [67]

Using a $\text{CO}+\text{H}_2+\text{C}_3\text{H}_6$ mixture as the reductant in cycling experiments, NO_x conversion was higher than with ammonia alone. Wang *et al.* concluded that propylene was an efficient reductant in the NSR-SCR combination. The results of a representative engine test over a high-emitting engine (called LR3) are given in Table 4. Though the SCR catalyst shows a non negligible activity in converting NMHC (non methanic HC) and CO, the greatest effect can be observed on the NO_x conversion. Only the LNT+SCR configuration allows to reach a good level of NO_x abatement.

Table 4: Emission results from FTP test (Federal test procedure) over the LR3 engine (code location: see Figure 6). Efficiency (%) represents the percentage of pollutant abatement (NMHC, CO or NO_x) at different stages of the exhaust pipe. From [67].

Emissions	Before DOC (FG) g/mile	After LNT (MB) g/mile	Tailpipe (TP) g/mile	DOC+LNT efficiency % (FG-MB)	SCR efficiency % (MB-TP)	Overall efficiency % (FG-TP)
NMHC	2.33	0.23	0.07	90	69	97
CO	6.42	0.30	0.21	95	30	97
NO_x	1.02	0.25	0.07	78	74	93

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) which shows higher performances than the catalyst of the first generation composed of Fe-BEA [66,67]. 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 operation.

The efficiency of Cu-BEA and Cu-ZSM5 as SCR catalyst coupled with Pt/BaO/Al₂O₃ was compared by De La Torre *et al.* in a very recent paper [68]. Both zeolites lead to very active co-catalysts in promoting the NO_x reduction by the NSR catalyst alone. The optimal Cu loading is obtained for 1.4%Cu in ZSM5 and 2.1%Cu in BEA (Table 5). Cu-ZSM5 and Cu-BEA can increase the NO_x conversion by 20-30% in the 200-300°C temperature range. A significant formation of ammonia is observed on the NSR catalyst alone which is used for the SCR reaction (a part of NH₃ being oxidized by O₂). Cu-ZSM5 and Cu-BEA have very similar effects so that activity per Cu ions appears higher over Cu-ZSM5.

Table 5: NO_x conversion, N₂, NH₃ and N₂O formation (expressed in N atoms) over the NSR catalyst alone and in the NSR+SCR configuration. Lean gas: 750 ppm NO+9.5%O₂ (balance in Ar). Rich gas: 750ppm NO+4%H₂ (balance in Ar). Cycles: 150 s lean/20s rich. Space velocity: 28600 h⁻¹ for NSR and 90000 h⁻¹ for SCR (1.4%Cu/ZSM5 or 2.1%Cu/BEA). From ref [68].

T (°C)	NSR alone				NSR+Cu-ZSM5 (left) and NSR+Cu-BEA (right)							
	NO conv %	N ₂ form %	NH ₃ form %	N ₂ O form %	NO conv %		N ₂ form %		NH ₃ form %		N ₂ O form %	
200	40.9	9.8	28.8	2.3	74.5	63.5	70.8	48.7	1.7	12.8	2.0	2.0
250	47.3	27.1	19.5	0.7	73.6	77.3	72.2	73.0	0.2	1.8	1.2	2.5
300	50.0	32.4	17.2	0.4	72.3	71.4	71.6	70.3	0.1	0.3	0.6	0.8
400	39.1	29.4	9.4	0.3	50.9	52.5	50.4	51.7	<0.1	0.1	0.5	0.7

The two zeolite catalysts were characterized by De La Torre *et al.* [68]. Total acidity is higher over BEA but ZSM5 shows a higher number of strong acid sites desorbing ammonia beyond 220°C. In the optimized catalysts (1.4%Cu-ZSM5 and 2.1%Cu-BEA), all the copper remains in the Cu²⁺ state. Increasing Cu loading leads to H₂/Cu<1 in TPR experiments, which confirms the formation of Cu⁺ and may be Cu⁰ species. Reduced species of copper appear to be less active and less selective to N₂ (higher formation of N₂O).

3.4. 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 [69,,71], the Group of Daimler AG [72,,75] and

others [76-78]. Fe-zeolite are generally found less active in SCR than Cu-zeolite catalysts at low temperatures (Fig. 7) but they would be more selective to N_2 . However, depending on the nature of the zeolite, contrasted results were obtained: for instance, Cu-ZSM5 was shown to be slightly more selective than Fe-ZSM5 when washcoated in dual layer monolith/NSR/SCR [79].

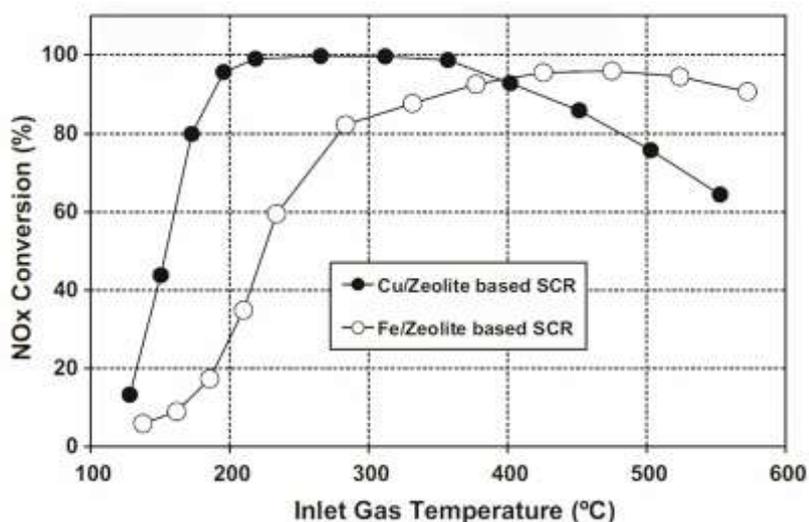


Fig. 7: NO_x conversion in NH₃-SCR over zeolite catalysts after hydrothermal ageing for 64h at 670°C. Reaction conditions: 350 ppm NO, 350 ppm NH₃, 14% O₂, space velocity: 30000 h⁻¹. From ref. [67]

Kinetic studies and specific experiments with designed reactants coupled to FTIR or DRIFT were mainly employed by Forzatti and coworkers to get detailed information about the behavior of each catalyst configuration (Pt-Ba/Al₂O₃ alone, Fe-ZSM-5 alone or Pt-Ba/Al₂O₃ + 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 the LNT catalyst 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 (physical mixture *vs* dual bed) and on the presence or not of CO₂ and H₂O in the gas mixture. Tables 6 and 7 summarize the result of Castoldi *et al.* [71]. 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. [63]. 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 6 and 7 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 6: 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. [71].

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 7: 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. [71].

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

The effect of the reactor configuration (dual bed vs physical mixture) seems to strongly depends on the temperature: in a preliminary study carried out at 200°C, Bonzi *et al* showed

that NO_x conversion was significantly higher in the physical mixture configuration, with 390, 610 and 980 μmol NO_x removed/g respectively after the NSR catalyst alone, after the NSR-SCR dual bed and after the physical mixture [69]. A comparison with the results of Tables 6-7 shows that the differences between the three configurations are more marked at 200°C than at 250°C.

Following their patent publication (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 [73,74]. 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. [72], is given in Table 8. 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 8). The same model (COMSOL package) was used to optimize the lean/rich cycle duration.

Table 8: 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. [72].

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. [80] 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 [78]. 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 H₂ concentration (3% in the conditions of ref. [78]) to get the highest NO_x conversion and the complete use of the ammonia produced in the NSR catalyst (no NH₃ slip). The specific role of H₂ concentration was also investigated by Lindholm et al. [76] who showed that the optimum H₂ 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 NO₂/NO ratio was a critical factor in the NSR-SCR coupling. There is a clear benefit when NO₂ is present in the feed at low temperatures. Model studies were recently performed by Kota et al who investigated the effect of exhaust pipe architecture (several sequential bricks LNT/SCR), the effect of the lean/rich cycle duration and the possible role of nonuniform noble metal loading [81]. The juxtaposition of two sequences of LNT/SCR bricks has a positive effect on NO_x conversion while nonuniform metal loading has only a minor effect. On the other hand, the lean/rich cycle duration has an important effect on the catalyst performance: reducing the cycle duration by a factor 2 can improve the NO_x conversion by about 15-20%.

3.5. Other systems including tungsten-based catalysts

Sullivan and Keane have proposed a system in which both NSR and SCR components are included in the same materials [82]. 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 NOx previously adsorbed on the catalyst, while gaseous ammonia is able to react with this stored NOx. Interestingly, Sullivan and Keane showed that N₂O was produced in the NH₃(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/Al₂O₃ with different potential SCR catalysts (Co/Al₂O₃, CuZSM-5, Ag/Al₂O₃) [64]. As expected (and already found in a previous work [63]), addition of Cu-ZSM-5 gave the highest performances. Excellent performances were also obtained with Co/Al₂O₃ while addition of Ag/Al₂O₃ 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.

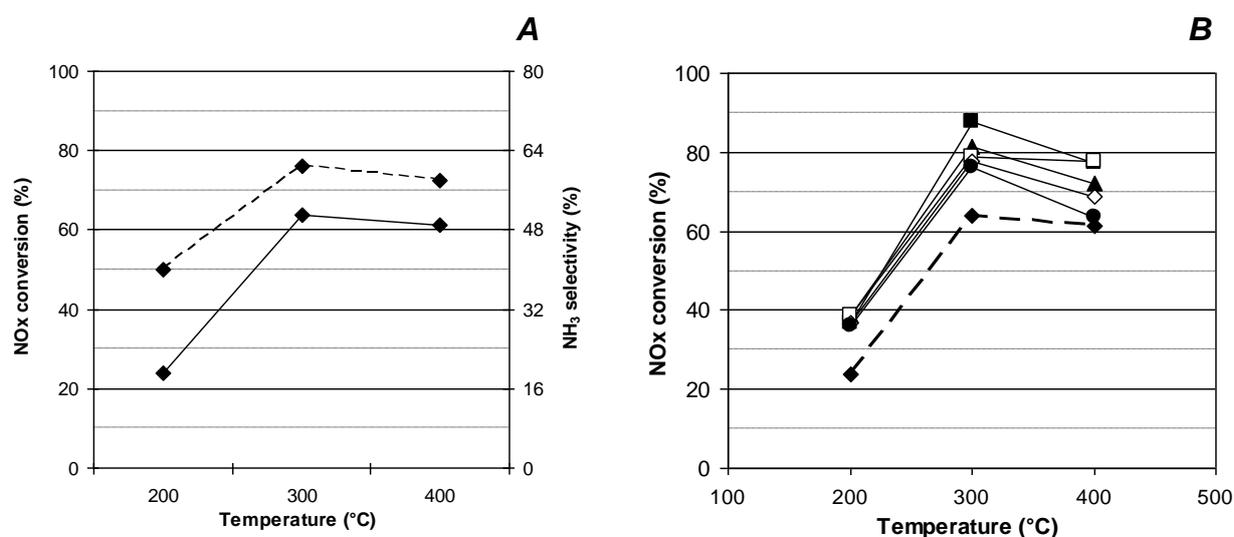


Figure 8: (A) NOx conversion (—) and NH₃ selectivity (--) over NSR Pt/Ba-Al model catalyst. (B) NOx conversion in NSR + SCR (NSR:SCR=60:120) combined system, from [83]:

(◆): Pt/Ba-Al; (■): Pt/Ba-Al + WO₃/Ce-Zr(20-80); (▲): Pt/Ba-Al + WO₃/Ce-Zr(40-60); (□): Pt/Ba-Al + WO₃/Ce-Zr(58-42); (◇): Pt/Ba-Al + WO₃/Ce-Zr(70-30); (●): Pt/Ba-Al + WO₃/CeO₂

Lean (60s): 500ppm NO + 10% O₂ + 10% CO₂ + 10% H₂O

Rich (3s): 3% H₂ + 10% CO₂ + 10% H₂O

Berland *et al.* also studied the combination of a model NSR catalyst (1%Pt/10%BaO/Al₂O₃, denoted as Pt/Ba-Al) with oxides-based SCR samples [84]. WO₃ supported over ceria-zirconia oxides (WO₃/Ce-Zr) were studied as the active NH₃-SCR catalysts. The effect of the

composition of the ceria-zirconia mixed oxides was studied with a constant WO_3 loading (10 wt% of W, added by impregnation). It is demonstrated that Pt/Ba-Al NSR catalyst can release important amount of ammonia, until over 50% of selectivity at 300°C (Figure 8A). SCR materials $\text{WO}_3/\text{Ce-Zr}$, with different Ce-Zr ratio, were associated downstream to the Pt/Ba-Al NSR catalyst. In the NSR+SCR combined system, the DeNO_x efficiency is strongly improved. An enhancement of 24 points in NO_x conversion was obtained at 300°C for the better SCR sample ($\text{WO}_3/\text{Ce-Zr}_{(20-80)}$) (Figure 8B) [83].

The acidic, basic and redox properties of the SCR catalysts were investigated. In fact, it is reported in Ref [85] that the redox properties are the key factors controlling the reactivity of the catalysts at low temperature, whereas at high temperature the acid properties are expected to play a major role in the SCR reaction. The addition of well dispersed surface WO_3 to $\text{CeO}_2\text{-ZrO}_2$ oxide led to an important NH_3 storage capacity (acidity) no present on the host support. In the same time, the addition of tungsten trioxide strongly decreased the oxygen mobility, the NO to NO_2 oxidation activity and NO_x storage capacity of ceria-zirconia oxides. The NO_x selective catalytic reduction with ammonia ($\text{NH}_3\text{-SCR}$) and the NH_3 selective catalytic oxidation with oxygen ($\text{NH}_3\text{-SCO}$) behaviours of these SCR samples have been also studied [83]. All $\text{WO}_3/\text{Ce-Zr}$ materials are active for reducing effectively the NO_x. These solids can reduce more than 80% of NO_x in $\text{NH}_3\text{-SCR}$ conditions including CO_2 and H_2O in feed gas. A strong oxidation of ammonia was also reported in absence of NO_x with nearly 80% of ammonia oxidized only into nitrogen.

Placed downstream to a model Pt/Ba-Al NSR catalyst, it was demonstrated that the NH_3 reactivity is temperature dependent. At low temperature (200°C) all the emitted ammonia from the NSR catalyst reacts (Figure 8C), but according only the standard $\text{NH}_3\text{-SCR}$. At higher temperature, fast $\text{NH}_3\text{-SCR}$ is then favoured due to the NO oxidation into NO_2 over the upstream NSR bed. Besides, at 300 and 400°C, a part of the stored ammonia is converted into

N₂ via the SCO reaction (Figure 9B). In addition, some NH₃ is released, especially for lower Zr contents in WO₃/Ce-Zr materials (WO₃/Ce-Zr₍₅₈₋₄₂₎ and WO₃/Ce-Zr₍₇₀₋₃₀₎). This result implies competitions between the NH₃-SCR and the NH₃-SCO reactions together with the formulation of WO₃/Ce-Zr SCR samples (Figure 9A and 9B). It also puts in evidence a lack of strong acid sites in order to store NH₃ at high temperature.

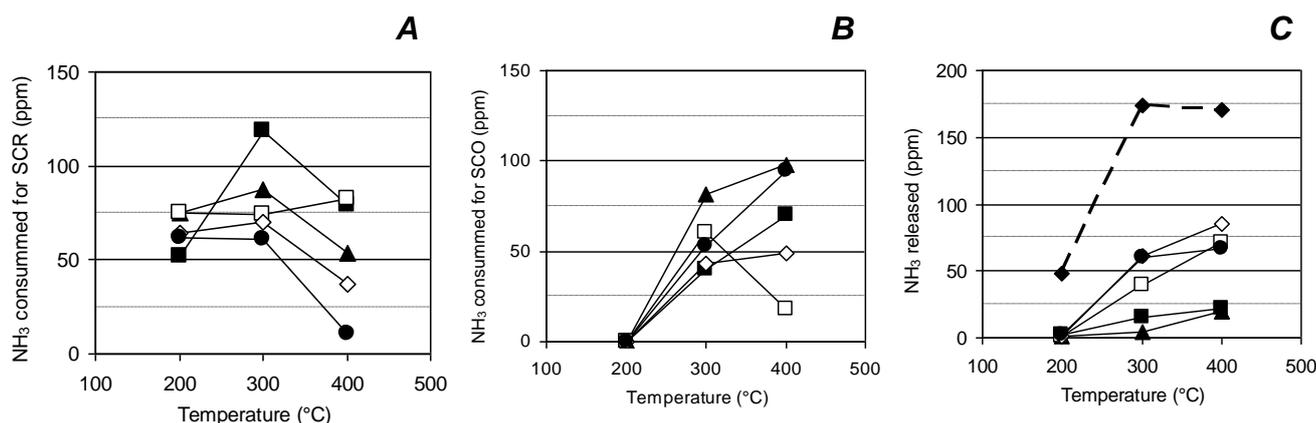


Figure 9: Ammonia consumption (ppm) on WO₃/Ce-Zr SCR catalyst in NSR + SCR (NSR:SCR=60:120) combined system for (A): NH₃-SCR, (B): NH₃ SCO and (C): unconverted NH₃. [83]

(◆): Pt/Ba-Al; (■): Pt/Ba-Al + WO₃/Ce-Zr(20-80); (▲): Pt/Ba-Al + WO₃/Ce-Zr(40-60); (□): Pt/Ba-Al + WO₃/Ce-Zr(58-42); (◇): Pt/Ba-Al + WO₃/Ce-Zr(70-30); (●): Pt/Ba-Al + WO₃/CeO₂

Lean (60s): 500ppm NO + 10% O₂ + 10% CO₂ + 10% H₂O

Rich (3s): 3% H₂ + 10% CO₂ + 10% H₂O

Finally the work of Kim *et al* about the HC-SCR and NH₃-SCR coupling system should be mentioned [86]. Although this study is out of the scope of the present chapter, 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 can be used in the second bed (CuCoY or Pd/Al₂O₃) in order to reduce the unconverted NO_x by ammonia.

4. Selective catalytic Reduction of NO_x by ammonia (NH₃-SCR)

As illustrated previously, materials associated downstream to the NSR catalysts are usually metal-exchanged zeolites [87], or more recently acidic ceria-zirconia based oxides as NH₃-SCR catalysts [83]. These samples have to be active in NO_x reduction by NH₃ together with a high ammonia storage capacity. Thus, zeolite type structure was largely studied in the coupling NSR + SCR system. More specifically, iron and copper are the main exchanged

metal in zeolites. Among the possible zeolites, ZSM-5 is one of the most studied materials in the academic literature, even if it is not the more appropriate structure.

4.1 Mechanistic aspects of the SCR reaction.

The reaction pathway of the NO_x selective catalytic reduction with ammonia (NH₃-SCR) is described by the following reactions (reactions 21-24):



These reactions are usually denoted as “standard” (21), “fast” (22), “NO₂-SCR” (23) and finally “slow” (24) SCR reactions [31,88-91]. It is usually established in the literature that SCR of NO_x with NH₃ occurs through an Eley-Rideal type mechanism [92-97], in which adsorbed ammonia reacts with weakly adsorbed NO or NO in the gas phase. Nevertheless, some studies suggest a reaction following a Langmuir-Hinshelwood mechanism [98-100]. However, it is currently received that SCR chemistry over metal-exchanged zeolite firstly requires the NO oxidation into NO₂, which is claimed to be the rate-determining step of the SCR mechanism [101]. For this reaction, metal-exchanged zeolites present largely higher activity than transition metal free zeolites [102]. It is also clearly evidenced that the NO₂/NO ratio is a key parameter for the SCR activity [88,89,103-105]. Indeed, fast SCR (reaction 22) and NO₂-SCR (reaction 23) reactions are much faster than the standard NO-SCR reaction (reaction 21). Note that in a NSR + SCR coupling system, the high oxidation activity of the Pt(RhPd)/BaO/Al₂O₃ NSR formulation also provides NO₂ by the oxidation of NO. Transition metal centers on zeolite are not only involved in the NO oxidation. For instance, it is suggested that iron species also promote the SCR reaction over zeolite framework in the case

of the Fe-exchanged ZSM-5 materials [106]. Especially, transition metal sites are claimed to promote the formation of reactive nitrates on the catalyst surface in the presence of gaseous NO₂ [107]. In fact, the formation of intermediate Feⁿ⁺-NO species (n = 2, 3), Fe²⁺(NO)₂ complexes, and NO⁺ are reported [108]. 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 [109]. Ammonium nitrate can also be formed according reactions 25-26:



In this later process, NH₃ is activated on zeolitic Brønsted acid sites, giving NH₄⁺ ions [110]. This point is discussed below (section 4.2). Ammonium nitrate thereafter decomposes into NO₂ and NH₃, as reported in reaction 27:



The combination of reactions (25) and (27) leads to the “fast” SCR, as reported above (reaction 22) [111].

However, if transition metal exchanged zeolites are active materials in NH₃-SCR, N₂O emission can be also observed. N₂O emission constitutes one of the main drawbacks of this system. For instance, Wilken *et al.* [112] 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 (reaction 28):



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) [113] (reaction 29). Mechanism involving NO (reaction 30) is proposed to occur at higher temperature (*i.e.* T ≥ 350°C) [114].



Finally, over Fe/MFI, and generally on zeolite, 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 [115]. This observation is consistent with SCR reactions described in reactions 21-23.

4.2 Effect of zeolite framework

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 [113,116]. Besides, it appears 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 [117,118]. 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 [119]. 3H-NH₄⁺ compound is also reported as an intermediate 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 [118]. 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 NO SCR 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 [120].

On the basis of these results, it appears that the activity of zeolite materials is associated with two main properties [121]:

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.

4.3 Role of acidic sites

The role of the acidic sites was studied by Brandenberger *et al.* [122] using 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 for NO SCR with NH₃. 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.* [123]. 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, FT-IR characterization of the ZSM-5 acidic properties shows that two types of hydroxyl groups are mainly detected, giving bands at 3720 and 3605 cm⁻¹ [124]. Thermal activation temperature strongly affects acidic properties. By increasing the temperature,

dehydroxylation of the zeolite is observed above 400°C. It induces 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) are studied in Ref. [125]. 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 to depend on the 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 [126]. 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.

In a comparative study of the NH₃-SCR reactions over a Cu-zeolite and a Fe-zeolite catalyst, Colombo *et al.* [127] observed that iron zeolite catalyst stores a lower amount of strongly bonded ammonia than copper zeolite (Figure 10). In addition, authors claim a greater activity in the ammonia oxidation reaction for the copper zeolite, together with a less sensitivity to the NO₂/NO_x ratio for the DeNO_x activity. Besides, N₂O is detected over Cu-zeolite even with negligible NO₂ feed content, whereas over iron zeolite, N₂O formation occurs only in excess of NO₂.

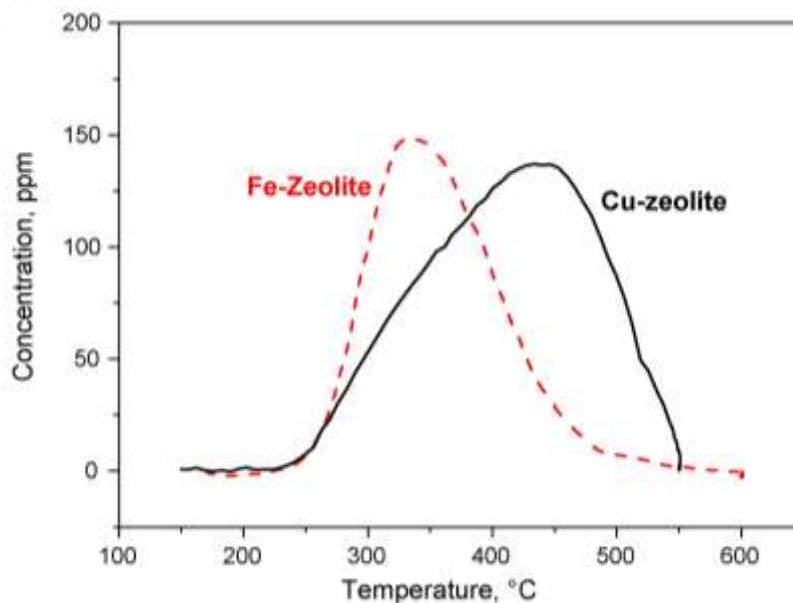


Figure 10: Ammonia TPD over Cu- and Fe-zeolite: $Q = 71 \text{ cm}^3/\text{min}$ (STP), $\text{H}_2\text{O} = 3\%$, $\text{O}_2 = 0\%$, $T \text{ ramp} = 15 \text{ K/min}$. Solid line = Cu-zeolite. Dashed line = Fe-zeolite. [127].

4.4 Active sites and performances of Cu-zeolite, Fe-zeolite and other systems in $\text{NH}_3\text{-SCR}$

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 the nature of the copper active site is strongly influenced by the reaction temperature and by the properties of the used zeolite. Indeed, over FAU zeolite, $[\text{CuOCu}]^{2+}$ dimer species are proposed to catalyze $\text{NH}_3\text{-SCR}$ reaction at low temperature ($T \leq 300^\circ\text{C}$) [128]. For NO decomposition, Moretti *et al.* [129,130] also proposed that the main active sites over ZSM-5 (silica to alumina ratio from 66 to 80) consist of dimeric Cu species strongly anchored to “next-nearest-neighbour” framework AlO_4^- species. On the opposite, Cu^{2+} is suggested to become active at higher temperature ($T \geq 350^\circ\text{C}$) over NaY [131,132].

At temperatures below 250°C , Sjövall *et al* [133] observed a beneficial effect of oxygen on the activity, contrary to higher temperatures. Ammonia slip is also affected by temperature. For instance, equal amounts of nitrogen oxides and ammonia are required at 175°C . In fact, over Cu-ZSM-5 the NO_x conversion is achieved by the reaction between NO_2 and adsorbed NH_3 . At higher temperature, ammonia oxidation occurs. However, if exposing the catalyst to

equimolecular amounts of NO and NO₂ increases the NO_x conversion, N₂O formation is furthermore observed.

Unfortunately, Cu-ZSM-5 catalyst suffers from thermal and water deactivation leading to segregation of extra-framework copper ions, and/or to the sintering of CuO-like species. To improve the durability or the low-temperature activity, Seo *et al.* studied the effect of ZrO₂ addition on DeNO_x performance of a SCR Cu-ZSM-5 catalyst [134]. It is reported that incorporation of the appropriate amount of ZrO₂ (2 wt%) increases the acid strength of acidic sites of catalyst which improved by 10-20% the NO_x conversion in the 200-300°C temperature range, as well as the durability of Cu-ZSM-5 catalyst. Recently Kwak [135] reports that Cu²⁺ ion-exchanged SSZ-13 (Cu-SSZ-13 with Chabazite (CHA) structure, containing small radius (3.8 Å) eight-membered ring pores), is more active and selective in reducing NO with NH₃ compared to Cu-ZSM-5 and Cu-beta. For instance, after hydrothermal treatment at 800°C for 16 h, Cu-SSZ-13 was found to show nearly no change in NO_x reduction activity, while Cu-ZSM-5 and Cu-Beta were found to lose NO_x reduction activity. In the same time, no significant rearrangement of nuclearity of copper active sites, of structural zeolite framework is observed on Cu-SSZ-13 compare to Cu-ZSM-5 after hydrothermal ageing.

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 [136,137]. 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 [136]. Small Fe_xO_y clusters like Fe₄O₄, isolated Fe²⁺ and Fe³⁺ ions, are also reported as possible active sites in the literature [138-141]. Besides, electron-deficient ferric oxide nanoclusters, isolated iron ions, and possibly oxygen-bridged iron binuclear complexes, may likewise coexist in Fe/MFI catalysts [142]. 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 [141]. In fact, the activity of Fe-ZSM-5 for SCR of NO by NH_3 is suggested to be catalyzed by different iron active species depending on temperature [143]. At temperatures below 300°C , the SCR activity was observed to be primarily caused by monomeric iron sites. At higher temperature ($T=300\text{-}500^\circ\text{C}$), the contribution of dimeric iron species, oligomeric species and partially uncoordinated iron sites become important. Fe-zeolite catalyst can also be sensitive to the NO/NO_2 ratio for NO_x removal via ammonia SCR [144]. The SCR efficiency was greatly enhanced when using pure NO_2 .

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 NO from the gas phase or weakly adsorbed NO [102]. 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 species. Nitrosamide species decomposes into nitrogen and water, while oxygen reoxidizes the catalyst surface [96]. Unfortunately, these catalytic systems remain poorly active at low temperature, and temperature higher than 350°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 ($150\text{-}250^\circ\text{C}$) [145]. However, the main drawback of these catalysts is the limited selectivity of the NO_x conversion into N_2 , with 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 [146,147]. 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 [148]. 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 [149]. 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 [148]. 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.

5. Conclusion and perspective

The combination of NO_x trapping materials with NH_3 -SCR catalysts for the NO_x treatment from mobile lean-burn engines has been reported. Particular attention has been paid in the 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 the 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 used as the reductant agent, water-assisted reaction, by hydrolysis of intermediate isocyanate species, is suggested. In the 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 involved in the NO_x reduction mechanism, by a sequential route in which NH_3 reacts faster with NO_x to yield N_2 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_3 yield.

Ammonia may likewise be used as reductant 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 NH_3 -SCR process. Iron-exchanged ZSM-5 has received much attention because of its promising activity and stability in the NH_3 -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 reductants, 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.

Furthermore, 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.

Finally, the literature essentially focuses on the association of NSR catalyst with usual NH_3 -SCR samples. However, in this coupled NSR+SCR system, ammonia is not directly injected in the feed gas, but produced during the regeneration step of the NSR process. The additional NO_x reduction occurs during the lean phases (in O_2 excess) between NO_x from gas phase and stored ammonia. It makes a prominent difference with the usual NH_3 -SCR technology. The development of specific SCR catalyst is desirable in a near future to achieved De NO_x efficiency and nitrogen yield even higher.

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