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Control of NO_x storage and reduction in NSR bed for designing combined NSR–SCR systems

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ABSTRACT

A detailed analysis of the catalytic behavior in the storage and reduction of NO_x of a homemade Pt–BaO/Al_2O_3 NSR monolith catalyst determining the N_2/NH_3 production surface in response to operational variables, namely temperature and hydrogen concentration during rich conditions was obtained. The production response curves are used to design the optimal operation, with high NO_x removal efficiency and maximum production of nitrogen, when running the single NSR catalyst and the combined NSR–SCR configuration with Fe-beta zeolite catalyst placed downstream the Pt–BaO/Al_2O_3 monolith. Optimal operation of the single NSR monolith was attained at 300 °C and 1% H_2, which showed NO_x removal of 74% with 64% of nitrogen production (both related to the total amount of NO in the feedstream, difference was mainly ammonia). The double NSR–SCR configuration allowed the Fe-beta catalyst storing ammonia to react with NO_x leaving the NSR during the subsequent lean phase. This has a benefit on both the NO_x removal efficiency and the N_2 production. The amount of ammonia needed for total NO_x removal efficiency and N_2 production can be supplied by tuning temperature and H_2 concentration. Temperature of 300 °C and 3% H_2 during rich conditions, produced 23% of ammonia at the exit of NSR. The SCR reaction between this amount of ammonia adsorbed on Fe-beta and the untrapped NO in NSR, resulted in practical total NO_x removal efficiency (98%) and N_2 production of 97% when the double NSR–SCR system is operated.

1. Introduction

It is now well recognized that diesel and lean burn engines improve fuel efficiency, consequently reducing emissions of carbon dioxide. However, the NO_x abatement from these engines is difficult to achieve since they work mainly under excess of oxygen. In the last decade, two main approaches towards NO_x reduction have been proposed: the NO_x storage and reduction (NSR) technology and the selective catalytic reduction (SCR) of NO_x.

The NSR catalysts consist of a cordierite monolith wash coated with a porous alumina on which alkali or alkali-earth oxide (e.g. BaO) and a noble metal (Pt) are deposited. These catalysts operate alternatively under lean and rich conditions [1,2]. During the lean period, when oxygen is in excess, the platinum oxidizes NO to a mixture of NO and NO_2 (NO_x), which is adsorbed (stored) on Ba as various species (nitrite, nitrate). Before that an unacceptable amount of NO_x slips through the catalyst, the engine switches to rich condition (excess of reductant) for a short period where the stored NO_x are released and reduced into N_2 over Pt. Different types of reducing agents such as hydrocarbon, CO, and H_2 have been used in NSR catalyst studies [3–6], and hydrogen has been found to be the most effective reductant.

On a commercial NSR system, the efficiency to transforming the emitted NO_x to N_2 should be as high as possible. This is remarkable, as the Pt itself is selective for the formation of N_2 from NO and H_2 only in a narrow range of NO to H_2 ratio. Nova et al. [7] concluded that the ammonia formation over Pt/Ba/Al was dependent on the amount of stored NO_x, temperature and hydrogen concentration. The reduction by H_2 of nitrates stored proceeds according to a two-step mechanism in which the first step is the fast reaction of hydrogen with nitrates producing ammonia, followed by the slower reaction of the latter with nitrate species leading selectivity to N_2 [8,9]. Accordingly a good tuning of the operating conditions of both the adsorption rate and the reduction phases can drive selectively to N_2 and/or NH_3.

The second approach, NH_3-SCR, is based on the selective catalytic reduction of NO_x by NH_3 generated by a urea solution stored in a special tank, or by NH_3 directly. This approach was originally developed for stationary emission sources, mainly power plants, but now is also a well established technique for truck and heavy duty vehicles, under the oxygen rich environment of diesel exhaust. In the urea-SCR technology, urea is injected in the flue gases where

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it decomposes and hydrolyzes to CO_2 and NH_3. The ammonia then reacts selectively with NO_x under lean (oxidizing) conditions, giving N_2 as the final product [10,11]. Non-noble metals like Cu, Fe and Ce over ZSM-5, are among the most active catalysts for the urea/NH_3-SCR process [12–14].

The performance of model Pt–BaO/Al_2O_3 NSR monolith catalyst under different operating conditions, including the duration of the regeneration and storage times, regeneration feed composition and temperature, and monolith temperature, has been recently reported in literature [6,15,16]. The cycled-averaged NO_x conversion exhibited a maximum at about 300–330 °C corresponding to the NO_x storage maximum. The N_2 selectivity exhibited a maximum at a somewhat higher temperature, at which point the NH_3 exhibited a minimum. We studied recently the influence of the duration of the storage and reduction periods, and the H_2 concentration on the NSR performance of a Pt–BaO/Al_2O_3 monolith catalyst [16]. Then, we defined the NSR efficiency as the moles of N_2 at the reactor outlet related to the total amount of NO_x entering the trap, expressed as percentage. Maintaining this efficiency as high as possible should be the aim of the NSR technology. At the studied conditions the minimum H_2 concentration to obtain total NO_x reduction during regeneration was experimentally determined (1.1% H_2), and also corresponded to the highest NSR efficiency, around 70%. If the H_2 concentration is lower or the reducing pulse is too short, the regeneration of storage sites is incomplete and thus the activity of NO_x trap decreases. On the contrary, if the H_2 concentration is higher or the pulse is too long undesirable product as ammonia is produced.

To avoid the NH_3 break-out, one possibility is to combine the NSR catalyst with a SCR system. Corbos et al. [14,17] found that the presence of a SCR catalyst placed downstream the NSR catalyst bed (double-bed configuration) allows the storage of ammonia released during the rich phase on the NO_x trap. The adsorbed ammonia is then converted to N_2 in the subsequent lean phase, according to the occurrence of a SCR reaction involving the stored ammonia and NO/NO_2 released from the front trap catalyst layer.

The objective of this paper is to find how the temperature and the reductant concentration can play jointly on NO_x removal efficiency when the NSR runs as a single system or combined with an NH_3-SCR downstream the NSR in a double bed configuration. We try to establish a completed picture of the $N_2/N_2O/NH_3$ distribution at the exit of the lean NO_x trap (NSR) in the temperature–H_2 concentration operational region. The N_2/NH_3 response surfaces will allow tuning the operational conditions in the lean NO_x trap with the aim of getting the required amount of NH_3 to react with NO/NO_2 in the downstream SCR bed improving the total efficiency of the double NSR–SCR configuration towards the desired N_2 product. This will increase both the NO_x removal efficiency and the N_2 selectivity of the process as well.

2. Materials and methods

2.1. Catalysts

The Pt–BaO/Al_2O_3 NSR catalyst was prepared from a cordierite monolith, 20 mm in length and diameter, with a cell density of 400 cells per square inch and a wall thickness of 150 μm. The monolith was wash coated with γ-alumina (163 $m^2\,g^{-1}$ after stabilization at 700 °C, 4 h) by several immersions of the monolith into the alumina slurry until ≈1 g Al_2O_3 was deposited in the monolith structure. The incorporation of platinum was carried out by adsorption from tetraammine platinum (II) nitrate solution supplied by Alpha Aesar and the excess of liquid remaining in the channels was blown out with compressed air. After calcination in air (500 °C, 4 h) and subsequent reduction of the metallic phase in a 5% H_2/N_2 stream (500 °C, 1 h), the barium was incorporated by immersion of the monolith in a barium acetate solution supplied by Aldrich. Finally, the catalyst was calcined again (500 °C, 4 h). More details on the preparation of the Pt–Ba/Al_2O_3 monolith catalyst can be found in our previous work [18].

The SCR catalyst was a homemade, powdered 2% Fe-beta zeolite catalyst. The beta-zeolite was supplied by Zeolyst International, pelletized, crushed and sieved to 0.3–0.5 mm to avoid mass transfer limitations. The catalyst was synthesized by the traditional ion-exchange procedure. Fe-ion exchange was carried out by dissolving the required amount of $Fe(NO_3)_3{\cdot}9H_2O$ in water, later zeolite was added to the solution (8 g/l) and was stirred for 24 h at 60 °C. The ion exchanged samples were then filtered, dried and calcined at 650 °C for 4 h before use. In order to characterize the Fe-beta catalyst several techniques such as BET surface area analysis, TEM, TPR, NH_3-TPD and XRD were employed. The fresh zeolite had a surface area of 535 $m^2\,g^{-1}$, which after iron incorporation was reduced to 464 $m^2\,g^{-1}$, probably due to the fact that some iron particles blocked the pores of the support. No signals related to iron species were detected in XRD. Fe_2O_3 particles around 10 nm were observed in the external surface of the zeolite by TEM. The catalyst had a total acidity of 0.24 mmol NH_3/g (determined by TPD) dominated by Brønsted type sites. For testing in double bed NSR–SCR configuration, the SCR catalyst powder (2.5 g) was loaded in a second tubular reactor placed after the NSR trap; the outlet of the NSR trap entering the SCR reactor.

2.2. NO_x removal experiments

The NO_x storage–reduction experiments for the single NSR configuration were performed in a vertical downflow stainless steel reactor, inside which the Pt–BaO/Al_2O_3 monolith was placed. When testing the double NSR–SCR configuration, the Fe-beta zeolite powder catalyst was packed in a second reactor connected downstream the NSR reactor. Temperature was measured by thermocouples at the top and the bottom of the NSR monolith, and in the bed of SCR catalyst. Streams from either the exit of the NSR monolith or the exit of the double NSR–SCR system can be addressed to analyzers.

The composition of the lean gas mixture for NO_x storage was 350 ppm NO and 6% O_2 using Ar as the balance gas. During the rich period oxygen was replaced by hydrogen maintaining 350 ppm of NO in the feedstream. The duration of the lean and rich periods (t_L = 150 s and t_R = 20 s, respectively) was maintained constant and controlled by two solenoid valves. Gases were fed via mass flow controllers and the total flow rate was set at 3365 ml min^{-1}, which corresponded to a space velocity of 32,100 h^{-1} for the NSR and 50,400 h^{-1} for the SCR. NO_x storage and reduction tests were carried out varying the catalyst temperature and the hydrogen concentration fed during rich period in the following intervals T = [100 °C, 420 °C] and C_{H_2} = [0.4%, 3.0%]. The experimental design was defined with 9 different levels for each variable, leading to a total of 9^2 = 81 experiments. Analysis of products after the Pt–BaO/Al_2O_3 monolith allowed us to determine the influence of each variable independently, maintaining the other constant, but also to construct the product distribution response surfaces (by interpolation) in the domain of both variables, temperature and hydrogen concentration.

The outlet gas concentrations, after the NSR monolith and after the double NSR–SCR configuration were continuously measured using a MKS MultiGas 2030 FT-IR analyzer with a specific oxygen detector (ZrO_2) totally integrated and a MKS Cirrus quadrupole mass spectrometer in line. NO, NO_2, NH_3, N_2O and H_2O were quantitatively monitored by FT-IR, whereas O_2 was measured by the ZrO_2 detector. On the other hand, H_2 and N_2 were qualitatively monitored by QMS and also O_2, the latter used to match accurately the corresponding data obtained from each instrument (FT-IR and QMS) in the concentration vs. time plots.

The NO_x removal efficiency of both single NSR catalyst and the combined NSR–SCR system is calculated from evolution of NO_x concentration with time, according to

$$\varepsilon_{NO_x} = \frac{F_{NO}^{inlet}(t_L + t_R) - \int_0^{t_L+t_R} F_{NO_x}^{outlet} dt}{F_{NO}^{inlet}(t_L + t_R)} \times 100 \quad (1)$$

The main response variable is the N_2 production related to the total amount of NO_x fed during lean and rich periods, i.e. the complete storage–reduction cycle

$$\pi_{N_2} \ (\%) = \frac{2N_2^{out}}{(NO^{in})_L + (NO^{in})_R} \times 100 \quad (2)$$

which has to be maximized either for the single NSR system or the double NSR–SCR configuration.

When designing the NSR–SCR double configuration, the NH_3 needed for the NO_x reduction in the SCR reactor has to be produced during the upstream NSR catalyst. In this case, it makes sense to account for the NH_3 production

$$\pi_{NH_3} \ (\%) = \frac{NH_3^{out}}{(NO^{in})_L + (NO^{in})_R} \times 100 \quad (3)$$

Eqs. (1) and (2) can be calculated from the areas under the NO_x, NH_3, N_2O and N_2 concentration vs. time curves. The closure of the nitrogen species balance was always verified with data obtained from the on-line FTIR and MS analyzers.

3. Results and discussion

3.1. NO_x removal and product distribution in single NSR reactor

This section reports the NO_x removal efficiency and N_2/NH_3 productivity obtained when only the Pt–BaO/Al_2O_3 monolith is used as a single NSR reactor. Fig. 1 shows two consecutive storage and reduction cycles once a steady cycle to cycle performance had been attained. The NO_x storage and reduction (NSR) operation was carried out at different operational conditions, defined by nine levels of temperature and nine levels of hydrogen concentration fed during the regeneration period as explained in Section 2. As an example, the NSR behavior of the catalyst when the operation was carried out at 180 °C and 3% H_2 is shown in Fig. 1a, whereas in Fig. 1b the operating conditions corresponded to 300 °C and 1% H_2.

During the 150 s long lean period the NO is partly oxidized to NO_2 and the NO + NO_2 (NO_x) mixture is adsorbed into the barium sites mainly as nitrites and nitrates [19]. Due to the fact that during all the lean period the NO_x concentration at the reactor exit resulted much lower than the inlet value (350 ppm) the storage capacity of the catalyst was proven. Moreover, although the operating conditions were different (180 °C, 3% H_2) and (300 °C, 1% H_2), the NO_x removal efficiency (ε_{NO_x}) calculated by Eq. (1), and representing the percentage of shaded areas in Fig. 1a and b related to the total NO fed at the inlet, resulted in similar values 76% and 74%, respectively. This fact can be explained taking into account independently the influence of temperature and hydrogen concentration in the NO_x storage and reduction behavior. On one hand, higher hydrogen concentration during the rich period improves the catalyst regeneration and consequently more adsorption sites are available for NO_x storage during the subsequent lean period, i.e. the higher the hydrogen concentration the higher the storage capacity is. On the other hand, the adsorption of NO_x shows a maximum situated at temperatures within range 250–350 °C [20–22]. The oxidation of NO to NO_2 considered as a previous step for NO_x storage is kinetically limited at lower temperatures, whereas the stability of the stored nitrates decreases with increasing the catalyst temperature above the aforementioned temperature range [2]. Consequently, it can be concluded that the operating conditions corresponding to 180 °C and 3% H_2 (Fig. 1a) favored the deep regeneration and limited the NO to NO_2 oxidation during the storage period. On the contrary, 300 °C and 1% H_2 (Fig. 1b) favored the NO to NO_2 oxidation and consequently the NO_x storage, but did not achieve such a deep regeneration. As a result, the mentioned opposite facts were equilibrated resulting in very similar NO_x removal efficiency in both situations.

Table 1
NO_x removal efficiency and N_2, NH_3 and N_2O production during NO_x storage and reduction for different operational conditions defined by points A, B, C, D and E.

Point	T (°C)	% H_2	ε_{NO_x} (%)	π_{N_2} (%)	π_{NH_3} (%)	π_{N_2O} (%)
A	180	0.55	48	34	7.9	5.2
B	180	3	76	33	42	1.6
C	380	0.55	31	28	1.2	0.34
D	380	3	70	53	16	0.17
E	300	1	74	64	9.5	0.31

Concerning the reduction period, significant differences can be observed in the concentration evolution with time of the nitrogen containing species. The NO_x stored during the lean period reacted with the inlet hydrogen to form N_2O, NH_3 or N_2 during the catalyst regeneration. When the NSR process was run at 180 °C and 3% H_2 (Fig. 1a) the concentration of N_2O and NH_3 was notably higher and, therefore, the production of nitrogen notably lower, comparing to that at 300 °C and 1% H_2 (Fig. 1b). As it is well known, increasing temperature and decreasing the hydrogen concentration fed during the catalyst regeneration, the product selectivity moves towards nitrogen. This trend can be explained based on mechanistic aspects of the reaction which have been already reported [8,9] and evidenced [6]. The nitrogen formation involves the occurrence of an in-series two step molecular process involving at first the formation of NH_3 upon reaction of H_2 with the stored nitrates, followed by the reaction of the so-formed ammonia with nitrates located downstream the H_2 front, that is, in a hydrogen free environment.

These two steps leading to final formation of nitrogen are influenced by the hydrogen concentration and temperature. As it can be observed in Fig. 1a, when 3% of H_2 was used during the regeneration period, the reductant was in such excess that H_2 was detected at the reactor outlet immediately after the regeneration period started. In that case, it can be deduced that the regeneration of the catalyst is carried out in a hydrogen rich environment. As a consequence, and considering that the reaction of H_2 with stored nitrates to form ammonia is much faster than the reaction of NH_3 with stored nitrates to form N_2 [23], ammonia is the main product of regeneration (Table 1, 180 °C and 3% H_2).

On the other hand, the NSR behavior shown in Fig. 1b, corresponding to 300 °C and 1% H_2, resulted in the same storage capacity during the lean period, as explained before, but changed notably the product distribution or selectivity. As it was expected, the increase in the operating temperature from 180 to 300 °C and the decrease in the hydrogen concentration fed during the rich period from 3% to 1% improved the formation of nitrogen.

The use of 1% H_2 to regenerate the catalyst resulted in an efficient NO_x storage and reduction. In contrast to the NSR operation carried out at 180 °C and 3% H_2, where H_2 is detected as soon as the regeneration period starts, operating at 300 °C and 1% H_2 resulted in nearly a total consumption of the inlet hydrogen, with very little amount of unreacted H_2 leaving the reactor just at the end of the regeneration period. It has been suggested that the regeneration of the monolith catalyst occurs progressively [23]. As the hydrogen front enters the catalyst, H_2 is completely consumed in the reduction of stored nitrates to form ammonia. Then, the ammonia formed in the initial part of the catalyst reacts with nitrates located downstream to form N_2 in a hydrogen free environment. Consequently, nitrogen is the first product detected

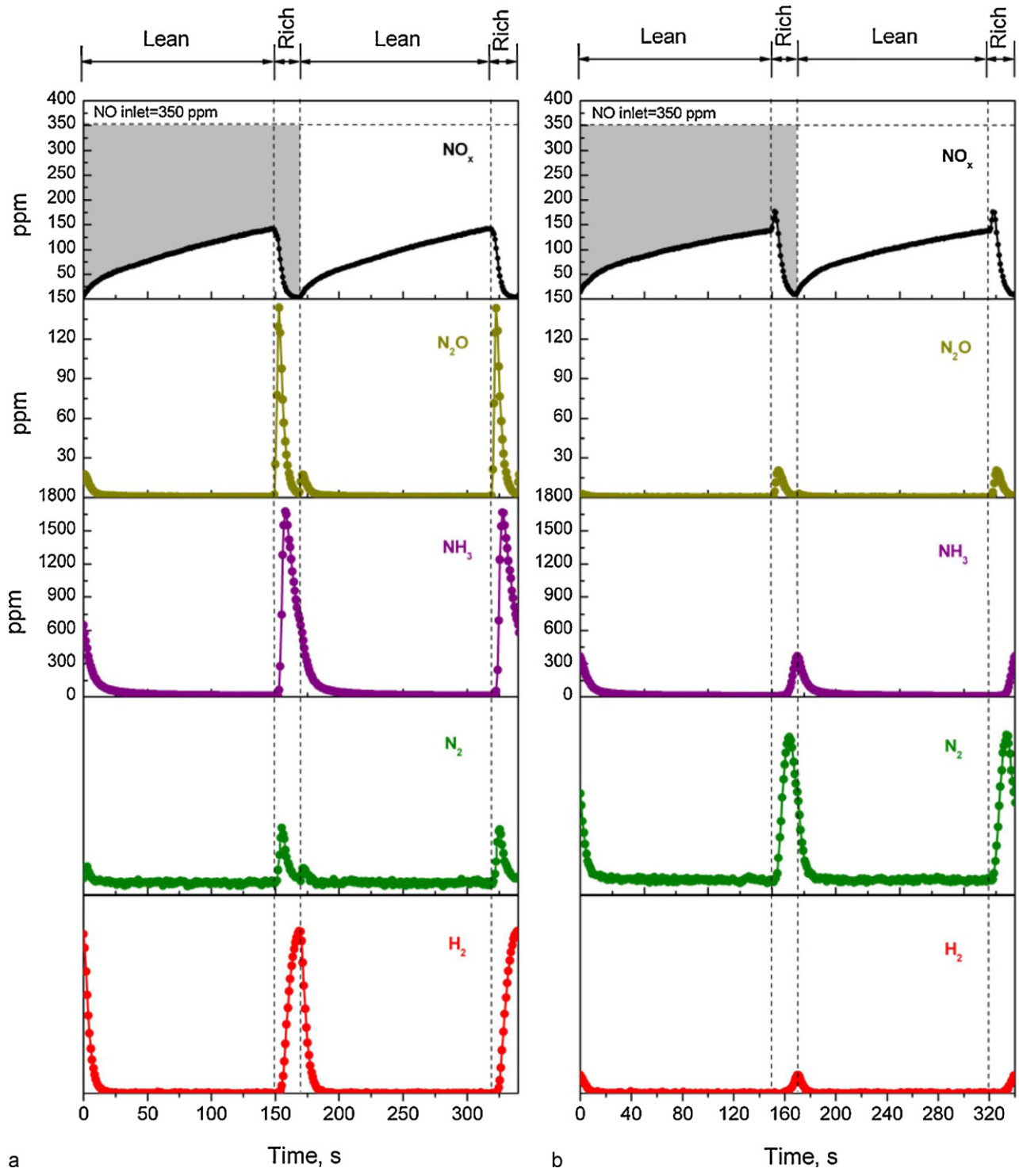

Fig. 1. Evolution of NO_x, N_2O, NH_3, N_2 and H_2 at the reactor exit during two consecutive storage and reduction periods: (a) 180 °C and 3% H_2; (b) 300 °C and 1% H_2.

at the outlet of the catalyst (Fig. 1b) along with a few ppm of N_2O (<30 ppm). Advancing with the regeneration time, the H_2 front progressively moves forward and finally reaches the catalyst end. In that situation, hydrogen reacts with stored nitrates located at the final part of the catalyst to form ammonia with no possibility to further react to form nitrogen. Therefore, the NH_3 unreacted at the last part of the regeneration period leaves the catalyst together with the H_2 breakthrough (Fig. 1b).

Up to now we have focused on mechanistic aspects of the reaction trying to understand the relation between the operational conditions running NSR catalyst and the product distribution, concluding that the operating conditions, i.e. temperature and hydrogen concentration, can be tuned in order to favor the formation of ammonia or nitrogen. As it has been shown in Fig. 1a, low temperature (180 °C) and high hydrogen concentration (3%), favored the production of ammonia. In fact, 42% of the inlet NO was converted into NH_3. On the other hand, intermediate temperature (300 °C) and an adequate concentration of H_2 (1%), neither in excess nor in defect, favored the nitrogen production (π_{N_2} = 64%, Table 1).

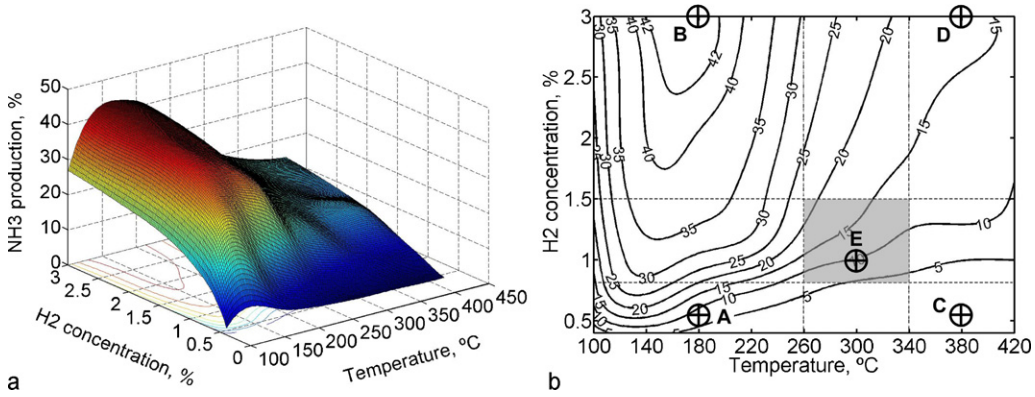

Fig. 2. (a) Ammonia production surface response in the temperature and hydrogen concentration domain during NO_x storage and reduction cycles. (b) Ammonia production isocurves projected to the temperature and hydrogen concentration space.

3.2. NSR conditions for designing double bed NSR–SCR configuration

The possibility of locating an SCR catalyst downstream the NSR can modify notably some aspects of the operation to reduce NO_x emission. It is worth to note that ammonia formed during the regeneration of NSR catalyst can be stored by a zeolite based SCR catalyst, reducing the ammonia slip. Furthermore, the reaction between the stored ammonia and the NO leaving the NSR catalyst without being trapped will increase the efficiency of the operation to convert more NO into nitrogen. Thus, it is important to determine the operational conditions running the NSR at which the ammonia production is notable and therefore the double bed NSR–SCR configuration will be beneficial compared to the single NSR configuration.

Fig. 2a shows the ammonia production (π_{NH_3}) surface response in the temperature and hydrogen concentration domain and Fig. 2b the isocurves corresponding to different levels of NH_3 production projected into the T–C_{H_2} bidimensional coordinates in the NSR trap. In Fig. 2b different points(A, B, C, D and E) are drawn corresponding to different operational conditions, and parameters describing the NSR behavior of each point are shown in Table 1.

Levels of hydrogen below 0.8% (A and C) are not recommendable to run the NSR process due to the fact that the reductant supply is in defect. Consequently, the catalyst cannot be properly regenerated and the resultant NO_x removal efficiency is low (48% and 31%, respectively). However, some differences can be observed with respect to temperature. At 180 °C (point A), production of NH_3 was 7.9%, whereas at 380 °C (point C) the ammonia production decreased to only 1.2%. The obvious result is that ammonia production is higher in the operating region defined by point A compared to point C. In fact, the possibility of obtaining ammonia production up to 25% in the operating region near point A, could make the combined NSR–SCR system suitable for improving the NO_x removal efficiency and selectivity to nitrogen. On the contrary, the ammonia production was lower than 5%in the operating region around point C. Therefore, the low amount of ammonia will probably not improve notably the efficiency of converting NO into N_2 in the combined NSR–SCR system with respect to run the operation in the single NSR reactor.

Moving to the region in which the supply of hydrogen is in excess during NSR regeneration, that is above 1.5% H_2, the picture is completely different. The increase in the storage capacity due to deep regeneration together with higher selectivity to ammonia moved the ammonia production to higher values. This is more evident at lower temperature, where the maximum ammonia production is obtained (42%), at 180 °C and 3% H_2 (point B). These operating conditions correspond to the NSR behavior shown in Fig. 1a. In the region including point B the ammonia production was higher than 30%. The ammonia production decreased as the temperature was increased. In fact, in the region including point D, the NH_3 production decreased to 10–20%.

Point E (300 °C and 1% H_2) corresponds to the intermediate position at which the NSR can operate efficiently, i.e. with high NO_x removal efficiency (74%) and maximum nitrogen production (64%), as we have previously reported [16]. Thus, these conditions are optimal to run the NSR catalyst in practical operation. Nevertheless, NH_3 production within range 5–20% was still present in the exhaust at point E and nearby (grey zone in Fig. 2). The use of this residual ammonia to reduce more NO_x in the double NSR–SCR configuration, improving in practice the NO_x removal efficiency and producing practically onlyN_2 at the exit, will be discussed in the next section.

3.3. Preliminary results in double bed NSR–SCR configuration

Once the NO_x removal efficiency and N_2/NH_3 production obtained with the single NSR catalyst have been understood when operating under different combinations of temperature and hydrogen concentration, we adapted a powder 2% Fe-beta zeolite catalyst (2.5 g) after the NSR monolith. First experiment was carried out at optimal conditions for single NSR, i.e. 300 °C and 1% H_2 (point E in Fig. 2). From this experiment it was determined that NH_3 production (9.5%) was not sufficient to reduce significantly the amount of NO_x at the outlet of the double NSR–SCR system. Then, with the aim of increasing the ammonia production, H_2 concentration was increased up to 3%, maintaining temperature at 300 °C, and practical total removal of NO_x and NH_3 was achieved, being totally converted to nitrogen. Results can be seen in Fig. 3, where black lines correspond to the single NSR bed, and red lines to the double NSR–SCR system.

When analyzing the results in Fig. 3, it is observed that the NO_x signal from the combined NSR–SCR system is notably lower during the lean period, practically zero until more than 100 s, arriving to 25 ppm at the end of the lean period, just before the switch to rich conditions. This means an exceptionally good NO_x removal efficiency of 98%, compared to 78% obtained with the single NSR catalyst (Table 2).

Table 2
NO_x removal efficiency and N_2, NH_3 and N_2O production for a single NSR or double NSR–SCR reactor configuration at 300 °C and 3% H_2.

Configuration	ε_{NO_x} (%)	π_{N_2} (%)	π_{NH_3} (%)	π_{N_2O} (%)
NSR	78	55	23	0.28
NSR–SCR	98	97	0.09	0.71

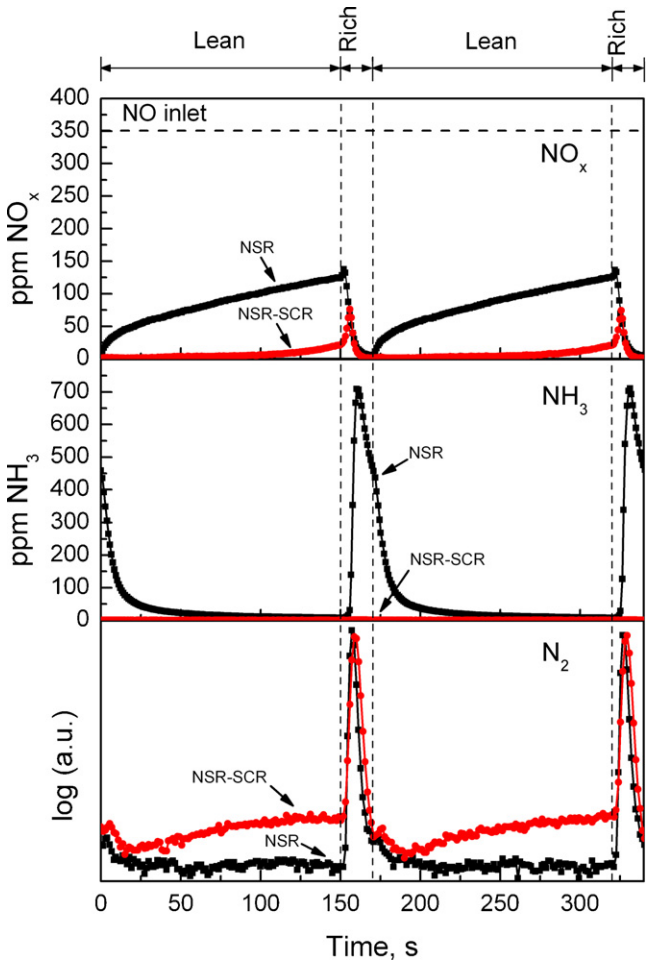

Fig. 3. Evolution of NO_x, NH_3 and N_2 at the reactor exit during two consecutive storage and reduction periods at 300 °C and 3% H_2 for a single NSR or double NSR–SCR reactor configuration.

The outlet ammonia concentration is also shown in Fig. 3. It can be seen that a large amount of ammonia was formed over the NSR catalyst, due to the excess of hydrogen fed during regeneration. The NH_3 concentration reaches 700 ppm during rich conditions over the NSR catalyst. However, almost no NH_3 is leaving when placing the SCR catalyst downstream of the NSR catalyst, along the total NO_x storage and reduction cycles.

The MS signal of nitrogen at the reactor outlet is also represented in Fig. 3. When using the single NSR catalyst, the signal of nitrogen was maintained practically constant during the lean period, while an appreciable increase in the production of nitrogen was observed for the double bed NSR–SCR system. For the combined system, the ammonia formed on the NSR catalyst during rich conditions is efficiently adsorbed on the SCR catalyst. Afterwards, when the gas mixture is switched to lean conditions, practically all NO is trapped on the NSR and consequently is not available to react with ammonia in the downstream SCR catalyst. As the NSR trap is becoming saturated, the NO/NO_2 concentration leaving the NSR is increasing and the nitrogen production over the SCR catalyst is promoted. This explains that formation of nitrogen follows a similar trend to that of NO_x leaving the NSR catalyst.

Hence, for the double bed NSR–SCR configuration, NO_x is removed via two routes during lean conditions: adsorption on the $Pt–Ba/Al_2O_3$ catalyst and reaction with NH_3 on the Fe-beta zeolite catalyst. Consequently, the outlet NO_x concentration is lower for the NSR and SCR system compared to the single NSR catalyst. This explanation is in agreement with previous studies [10,17,24].

The SCR process is based on the following reactions between NH_3 and NO/NO_2:

$$2NO + 2NH_3 + 1/2O_2 \rightarrow 2N_2 + 3H_2O \quad (4)$$

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \quad (5)$$

The so-called "standard SCR" and "fast SCR" reactions, Eqs. (4) and (5), respectively, lead to formation of nitrogen by reaction between equimolecular amounts of NO_x and NH_3. In our experimental conditions (300 °C, 3% H_2), 31 μmol NH_3 are produced during NSR regeneration and stored over the SCR catalyst. Likewise, during the lean period 36 μmol NO_x go through the NSR without being trapped. Hence, the amount of NH_3 is in defect for equimolecular reaction giving the difference of 5 μmol NO_x which can be observed at the outlet of the NSR–SCR system in Fig. 3.

Total NO_x removal with total selectivity to N_2 could be achieved in the double NSR–SCR configuration if operational conditions are chosen to allow equimolecular reaction between NO_x and NH_3 during lean conditions over the SCR catalyst. In our system, experiments carried out at 250 °C and 3% H_2 (not shown) gave total removal of NO_x and 100% selectivity to N_2 as the requirement of NO_x/NH_3 equimolecularity was achieved. At present, deeper analysis of different conditions and configurations are being further investigated in our laboratories.

4. Conclusions

In this work the reduction of NO_x over the single $Pt–BaO/Al_2O_3$ NSR monolith was investigated for different combination of temperature and hydrogen concentration fed during rich conditions. The aim was to get understanding of the single NSR process to be applied when designing the double NSR–SCR configuration.

On a commercial NSR system the efficiency to transform the emitted NO_x to N_2 should be as high as possible. High NO_x removal efficiency (74%) with maximum nitrogen production (64%) was obtained at 300 °C and 1% H_2 during the rich period, but also 9.5% of ammonia was produced. At lower temperature and higher H_2 concentration the production of ammonia is significantly increased, which is the basic limitation of NSR catalysts. On the double bed NSR–SCR configuration, the increase of H_2 concentration to 3% during NSR regeneration enhanced the SCR reaction between the ammonia adsorbed on Fe-beta and the untrapped NO leaving the NSR catalyst, resulting in NO_x removal efficiency of 98% and N_2 production of 97%.

Summarizing, the exact knowledge of the N_2/NH_3 production through the operational maps shown in this work for NSR catalyst with respect to temperature and reductant amount during rich conditions is essential for designing of very efficient combined NSR–SCR systems. Obviously, also the efficiency of the downstream SCR catalyst has to be optimized to be coupled with NSR behavior, which is being at preset the object of our further investigation.

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