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NO_x removal efficiency and ammonia selectivity during the NO_x storage-reduction process over Pt/BaO(Fe, Mn, Ce)/Al₂O₃ model catalysts.

Part I: influence of Fe and Mn addition.

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Abstract

NO_x storage-reduction process was studied using lean/rich cycling condition over Pt/BaO/Al₂O₃ model catalyst, with a special attention to the ammonia emission. The NO_x reduction selectivity strongly depends on the hydrogen conversion introduced during the rich pulses. NH₃ is emitted while hydrogen is not fully converted. It was concluded that the NH₃ formation rate via the NO_x reduction by H₂, is higher than the NH₃ reaction rate with NO_x to form N₂. The effect of H₂O and CO₂ on the reduction step were also examined and results were explained mainly taking into account the reverse water gas shift reaction.

Fe addition in Pt/BaO/Al₂O₃ leads to a strong deactivation of the catalyst, probably due to interaction between iron and platinum. Mn is a poison for the reduction step at 200 and 300°C, but it significantly enhances the NO_x reduction at 400°C (conversion and selectivity). Mn favors the NO_x reduction with ammonia, even if the introduced hydrogen is not fully converted.

Keywords: NO_x storage; NO_x reduction; ammonia; barium; lean/rich cycles; manganese; iron.

1. Introduction:

Lower CO₂ emissions from automotive sources are necessary and lead to the development of diesel and lean-burn engines. However, exhaust gases from these engines contain NO_x in excess of O₂, which makes NO_x reduction into N₂ very difficult. One possible way to reduce NO_x emissions is to use a NO_x storage reduction (NSR) catalyst [1]. It works mainly in lean condition, and the NO_x are then oxidized on precious metals and stored on basic compounds, mainly as nitrates. Periodically, the catalyst is submitted to rich conditions for few seconds, and the nitrates previously formed during the lean step are reduced into N₂ on the precious metals [2,3]. Platinum on alumina based catalysts are the most investigated systems and barium oxide is usually added as NO_x storage material. One of the disadvantages of this catalyst is the deactivation, mainly due to sulfur poisoning [4,5,6], and to thermal aging [6,7,8]. Moreover, another problem arises from ammonia emissions. Indeed, NH₃ can be formed during short excursions under rich conditions which are necessary to reduce trapped NO_x species [9,10].

The aim of this work is mainly focused on this ammonia emission. NH₃ and N₂O are both undesirable products which can be observed during the NO_x reduction [11,12,13]. Ammonia formation is favored when H₂ is used as reducer, whereas N₂O is obtained with CO as reducer [13,14]. Several publications also showed that NH₃ selectivity increases with temperature [13,15,16]. However, in these studies, neither H₂O nor CO₂ were included in the reaction mixture. On the contrary, with H₂O and CO₂ in the gas mixture, Pihl et al. [17] and Lindholm et al. [18] have observed a higher NH₃ emission at low temperature. Ammonia selectivity increases with the increase of the H₂ concentration [17,18]. According to Lesage et al. [19,20] and Castoldi et al. [21], the NO_x trap regeneration leads to N₂ firstly, and NH₃ is formed with reducer progress through the catalytic bed. Pihl et al. [17] have proposed that the stronger adsorbed NO_x are responsible for the ammonia formation. Indeed, these species are submitted to more reducing atmosphere since there are still on the catalysts after the beginning of the rich period (near no more residual O₂ is present). This hypothesis is consistent with the increase of the NH₃ selectivity with the Ba loading increase [21] since it allows the formation of stable bulk barium nitrates [22]. Finally, NH₃ is assumed to play an important role in the NO_x trap regeneration. However, some points are still in opposition.

The objective of the study is to have a better understanding of the ammonia emission on Pt/BaO/Al₂O₃ model catalysts. Particularly, we have varied the catalytic test conditions in order to put in evidence the conditions of ammonia emission and its possible role in the NO_x reduction. Moreover, we have studied the influence of CO₂ and H₂O on the NO_x storage-reduction efficiency, as we have previously done for the NO_x storage step [23].

In this first part, we have also examined the effect of two commonly added transition metals in NSR system: iron and manganese. A second part will discuss with cerium and Ce-Mn addition. Mn is known to be active in NO oxidation [24,25,26], a crucial step for the storage process. Moreover, Mn can also participate to the NO_x storage [26,27] and exhibits an activity in the NO_x reduction by NH₃ reaction [28,29,30,31]. Fe is generally added in NSR formulations to improve the catalyst sulfur resistance. Iron oxide is reported to inhibit the bulk barium sulfates formation [32,33]. Fe is also reported to be active in NO_x SCR by ammonia [30].

In a previous work, we have shortly studied 1%Pt/10%BaO/Al₂O₃ systems modified by Mn or Fe addition [34]. These preliminary results showed that Fe led to a better sulfur elimination due

to bulk barium sulfate formation inhibition as already reported, but the NO_x storage property was not fully recovered. Moreover, Fe addition induced rather a degradation of the NO_x conversion under rich/lean cycling conditions at high temperature (400°C). Mn addition also improves the NO_x storage capacity, but no significant influence on the sulfur elimination was observed. Compared with 1%Pt/10%BaO/Al₂O₃, the Mn-doped catalyst exhibited slightly lower NO_x conversion but the NH₃ selectivity was drastically decreased at 400°C. Additional test showed that the NO_x conversion could be improved over the Mn-based catalyst by increasing H₂ concentration in the rich pulse.

In this new study, catalysts were loaded with 20% BaO and catalytic tests and characterizations were done in order to have a better understanding of the role each component, especially toward NH₃ emission.

2. Experimental:

2.1. Catalysts preparation

The reference catalyst contains 1wt% Pt and 20wt% BaO on alumina. In addition, the modified samples contain 7.2wt% Mn or 7.0wt% Fe, corresponding to a "additive/Ba" molar ratio of 1. Ba and additives were deposited by co-precipitation. Alumina powder (230 m².g⁻¹) was suspended in a solution at 60°C and pH 10, in order to ensure complete precipitation of the barium and transition metal. The nitrate salts of the desired compounds (Ba^{II}, Mn^{IV}, Fe^{III}) were then added under vigorous stirring, and the pH was maintained constant by ammonia addition. After 30 min, the solution was evaporated at 80°C under air and the resulting powder was dried at 120°C. After calcination at 700°C, platinum (1wt%) was impregnated using a Pt(NH₃)₂(NO₂)₂ aqueous solution. After drying, the catalyst was pre-treated at 700°C for 4h under N₂, and finally stabilized at 700°C for 4h under a mixture containing 10% O₂, 5% H₂O in N₂. As previously reported [35], the intermediate nitrogen treatment allows a higher platinum-barium dispersion. The obtained catalysts are noted Pt/20Ba/Al, Pt/20BaFe/Al and Pt/20BaMn/Al. They exhibit BET specific surface areas of 127 m².g⁻¹, 118 m².g⁻¹ and 115 m².g⁻¹, respectively. In addition, the influence of manganese loading was studied. The Mn/Ba molar ratio (noted X in Pt/20BaMnX/Al notation) was varied between 0.1 and 1.5 using the same preparation protocol. For all samples, the platinum dispersion, deduced from H₂ chemisorption measurements, varies between 8 and 11%.

2.2. Catalyst characterizations

The BET surface areas were deduced from N₂ adsorption at -196°C carried out with a Micromeritics apparatus. Prior to the measurement, the samples were treated at 250°C under vacuum for 8 h to eliminate the adsorbed species.

The platinum dispersion was determined using the H₂ chemisorption method. After *in situ* reduction under pure hydrogen at 500°C for 1h, the sample was flushed at the same temperature under argon for 3h. The hydrogen was dosed on the sample at room temperature until saturation. After flushing under argon for 10 min, the sample was exposed to hydrogen again. The amount of chemisorbed hydrogen was taken as the difference between the two hydrogen exposures.

X-ray powder diffraction was performed at room temperature with a Bruker D5005 using a $K\alpha$ Cu radiation ($\lambda=1.54056 \text{ \AA}$). The powder was deposited on a silicon monocrystal sample holder. The crystalline phases were identified by comparison with the ICDD database files.

2.3. Catalytic activity measurements

2.3.1. NO_x storage capacity (NSC) measurement

Before the NO_x storage capacity measurements, the catalyst (60mg) was pretreated in situ for 30 min at 550°C, under a 10% O₂, 10% H₂O, 10% CO₂ and N₂ mixture (total flow rate: 10 L.h⁻¹), and then cooled down to the storage temperature under the same mixture. The sample was then submitted to a lean mixture as reported in Table 1, at 200°C, 300°C and 400°C. The gas flow was introduced using mass-flow controllers, except for H₂O which was introduced using a saturator. Both NO and NO_x concentrations (NO+NO₂) were followed by chemiluminescence. H₂O was removed prior to NO_x analysis with a membrane dryer. Long time storage is not representative of the NSR catalyst working conditions, since the lean periods are commonly around 1 min. The NO_x storage capacity was then estimated by the integration of the recorded profile for the first 60 seconds, which corresponds to the lean periods of the NSR test in cycling conditions. The contribution of the reactor volume is subtracted. With the conditions used in this test, 57.4 $\mu\text{mol NO}_x$ per gram of catalyst are injected in 60s. For easier comparisons with the NSR tests, results are expressed as the NO_x storage rate (%) for 60s ($\mu\text{mol}_{\text{stored NO}_x} \text{ g}^{-1}_{\text{cata}} \times 100 / 57.4$) In addition, the platinum oxidation activity was estimated as the NO₂/NO_x ratio (%) at saturation (usually about 900s).

Table 1: Rich and lean gas compositions used for the NO_x conversion test (60s lean / 3s rich). Lean mixture was used for the NO_x storage measurements. Total flow rate: 10 L h⁻¹.

Gas	NO	H ₂	O ₂	CO ₂	H ₂ O	N ₂
Rich	-	1 to 6%	-	10%	10%	Balance
Lean	500ppm	-	10%	10%	10%	Balance

2.3.2. NO_x conversion in cycling conditions (NSR test)

Before measurement, the catalyst (usually 60mg if no other indications are given) was treated in situ at 450°C under 3% H₂, 10% H₂O, 10% CO₂ and N₂ for 15 min. The sample was then cooled down to test temperatures (200, 300 and 400°C) under the same mixture. The NO_x conversion was studied in cycling condition by alternatively switching between lean and rich conditions using electro-valves. The lean and rich periods are 60s and 3s, respectively. The gas composition is described in Table 1. Note that only the stored NO_x during the lean periods can be reduced using this procedure since there is no reducer in the lean mixture and no NO_x in the rich one. NO and NO₂ were followed by chemiluminescence, N₂O by specific FTIR, H₂ by mass spectrometry. Before the analyzers, H₂O was removed in a condenser at 0°C. For each studied temperature, the activity of the catalysts was followed until stabilization. After

stabilization, the outlet water was condensed for one hour in a dry condenser and then analyzed by two different HPLC. One is used for NH_4^+ analysis, which allows calculating the ammonia selectivity, and the other one for NO_2^- and NO_3^- which were added to the unconverted NO_x . The N_2 selectivity is calculated assuming no other N-compounds than NO , NO_2 , N_2O , NH_3 . Some tests were also performed using a Multigas FTIR detector (MKS 2030) without water trap system and same results were then obtained.

3. Results

3.1. Pt/20Ba/Al catalyst

3.1.1. XRD Characterization.

The X ray diffractograms obtained with reference Pt/20Ba/Al before and after the platinum impregnation step are reported in Figure 1. The main crystallized phases detected by X-ray diffraction are BaCO_3 and BaAl_2O_4 . However, as previously mentioned [35] some phase transformation occurred during the platinum addition. Indeed, the XRD pattern of the powder obtained before the platinum impregnation steps exhibits significantly more intense BaCO_3 and BaAl_2O_4 diffraction peaks than for Pt/20Ba/Al. It can be attributed to barium leaching from the support during the platinum impregnation step [36,37]. Note that with a lower barium loading (10%), the same trend was observed for BaAl_2O_4 , but BaCO_3 peaks were nearly not detected before the platinum impregnation [33].

Figure 1: X ray diffractograms obtained with Pt/20Ba/Al (a) and with the same sample before the platinum impregnation step (b): (#) BaCO_3 , (*) BaAl_2O_4

3.1.2. NO_x storage capacity / NO_x conversion in cycling conditions

In this section, NO_x storage capacity and NO_x conversion in cycling conditions (NSR test) were measured with the reference catalyst Pt/20Ba/Al. The effects of H_2O and CO_2 in the gas mixture were evaluated in regard of the catalytic behaviors. The reducer concentration (H_2) was also varied during the reduction steps of the NSR process. The aim of this section is to have a

better understanding of the NSR mechanism with the reference catalyst, especially toward the possible ammonia emission.

3.1.2.1. Pt/20Ba/Al behavior using the reference mixture

NO_x storage capacities of platinum-barium supported catalysts were extensively studied in previous works in our laboratory [5,23,34,35]. However, new measurements were done using the same duration (60s) and the same gas composition as the lean periods of the cycled NO_x storage/reduction catalytic test. Results are expressed as NO_x storage rate (%) for each tested temperature (Table 2). Using the complete reaction mixture (with CO₂ and H₂O), the NO_x storage capacity of Pt/20Ba/Al increases with the temperature test, from 57% at 200°C to 83% at 400°C. Then, whatever the temperature test, the inlet NO_x is not totally stored in 60s.

The NSR properties of this catalyst are reported Table 2 (complete mixture). First, note that N₂O was never significantly observed during these tests in cycling condition, whatever the tested catalyst and the conditions test. This point is consistent with the study of Abdulhamid et al. [13] who claim that N₂O is mainly obtained with CO as reducer. Whatever the tested temperatures, the NO_x conversion is always lower than the NO_x storage rate for 60s (Table 2). The maximum NO_x conversion is obtained at 400°C and reaches only 45%. In addition, the ammonia selectivity is rather high. It reaches around 20% at 200 and 300°C and 33% at 400°C. In the same time, only 70 to 90% of the introduced hydrogen is converted. Thus, reducers remain (H₂, NH₃), whereas only around half of the stored NO_x reacts. The limiting step of the process is then the reduction step.

Table 2: Pt/20Ba/Al catalyst: Influence of H₂O and CO₂ on the NO_x storage rate (%) for 60s (catalyst (60mg) is submitted to 57.4 μmol_{NO_x}/g in 60s) and on the NSR test: NO_x conversion rate, NH₃ selectivity and H₂ conversion (%).

Temperature test (°C)	Reaction mixture	NO _x storage test	NSR test	
		NO _x storage rate (%)	NO _x conv. (%)	NH ₃ select. (%)
200	complete	57	35	22
200	without H ₂ O	73	21	17
200	without CO ₂	81	65	18
300	complete	73	29	21
300	without H ₂ O	89	31	24
300	without CO ₂	78	54	10
400	complete	83	45	33
400	without H ₂ O	98	41	41
400	without CO ₂	100	70	12

In opposition with the storage tests, the minimum NO_x conversion is observed at 300°C. This can be attributed to the balance between the NO_x desorption rate and the NO_x reduction rate. At low temperature (200°C), the NO_x desorption during the rich pulses should be low but the NO_x reduction rate is low too. At 300°C, the storage capacity increases but the NO_x conversion is lower compared with 200°C. This observation can be attributed to a higher NO_x desorption rate whereas the reduction rate should not increase in the same proportion. At 400°C, the NO_x desorption should increase again, but the reduction rate is then high enough to obtain a NO_x conversion rate higher than those observed at 200°C or 300°C.

3.1.2.2. Influence of H₂O and CO₂

As already reported for 100s storage [23], tests without water or carbon dioxide lead to enhancements of the NO_x storage capacities (Table 2). H₂O was found to inhibit the NO to NO₂ oxidation. Indeed, the NO₂/NO_x ratios after storage saturation with water in the feed stream are 9%, 21% and 42% at 200, 300 and 400°C, respectively. Without H₂O in the feed stream, they reach 18%, 30% and 48%, respectively.

The inhibiting effect of CO₂ on the NO_x storage is stronger compared with the H₂O inhibiting effect. When CO₂ is removed from the feed gas, near all the introduced NO_x are trapped at 300 and 400°C (Table 3). CO₂ has no influence on the NO to NO₂ oxidation rate and the inhibiting effect of CO₂ on the NO_x storage was attributed to a competition between nitrates and carbonates formation on the storage sites [23].

Results of the NO_x storage/reduction tests without H₂O or CO₂ are also reported in Table 2. In opposition with the storage tests, absence of water leads to a deterioration in the NO_x reduction rate, especially at 200°C, from 35 to 21%. At the same time, higher ammonia selectivity is observed in absence of water. On the contrary, tests without CO₂ show a significant increase of the NO_x conversion. Moreover, NH₃ selectivity is also lowered especially at 300 and 400°C. In fact, addition of CO₂ induces losses between 35 and 45% whereas the losses are between 20 and 30% for the NO_x storage. Thus, CO₂ also inhibits the reduction step. It can be attributed to a higher NO_x desorption rate during the rich pulses when CO₂ is added in the reaction mixture [38], leading to higher NO_x slip. Whatever the test condition, note that the introduced hydrogen is still never fully converted.

However, all these results can be mainly explained taking into account the reverse water gas shift reaction (RWGS, $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$) and its consequence on the NH₃ formation pathway proposed by Lesage et al. [19,20], i.e. the hydrolysis of isocyanate Al-NCO and Ba-NCO species ($2 \text{NCO} + 3 \text{H}_2\text{O} \rightleftharpoons 2 \text{NH}_3 + 2 \text{CO}_2 + \frac{1}{2} \text{O}_2$).

Absence of water favors the H₂ conversion into CO (confirmed by CO detection, until 350 ppm at 400°C), which is less active than H₂ for NO_x reduction at low temperature [1]. Moreover, CO is a precursor or the isocyanate species, which can also explain the higher ammonia selectivity in absence of water in the feed stream.

Without CO₂ in the feed stream, H₂ conversion into CO is not possible, which is favorable for the NO_x reduction. Another consequence is that the formation of isocyanate species is not expected since there is no other carbon source in the used reaction mixture. However, even if the NH₃ selectivity is dramatically lowered in absence of CO₂, this compound is still significantly detected. Then the isocyanate pathway is not the only one to form NH₃.

Finally, water induces a positive effect on the reduction step (conversion and selectivity), by limiting the hydrogen transformation into CO via the reverse WGS. On the contrary, CO₂ favors the fast NO_x desorption during the rich pulses and promotes the hydrogen transformation into CO which is less efficient for the NO_x reduction and leads to higher ammonia formation rate via the isocyanate pathway.

All other results in this study were obtained with both H₂O and CO₂ in the feed stream.

Table 3: NO_x storage rate (%) for 60s. Catalyst (60mg) is submitted to 57.4 $\mu\text{mol}_{\text{NO}_x}/\text{g}$ in 60s. Influence of H₂O and CO₂ for Pt/20Ba/Al catalyst.

Storage Temperature	NO _x storage rate (%)		
	200°C	300°C	400°C
Catalyst			
Pt/20Ba/Al	57	73	83
Pt/20BaFe/Al	58	73	85
Pt/20BaMn/Al	61	74	84

3.1.2.3. Influence of the hydrogen concentration in the rich pulses

First, preliminary tests were performed in order to estimate the hydrogen consumption due to the mixing of the lean and rich periods compared with the H₂ consumption used for the NO_x reduction. Tests were carried out with 3% H₂ in the rich pulses, but without NO_x in the lean periods. Unfortunately, it was observed that the H₂ consumptions are similar with or without NO in the lean periods. As a consequence, it can be deduced that (i) a large part of the reducing agent can react with oxygen, indicating the mixing of the rich and lean mixtures; (ii) it is not possible to evaluate the H₂ consumption linked with the NO_x reduction when the complete mixture is used; (iii) H₂ should react preferentially with the stored NO_x rather than with the remaining oxygen from the lean periods.

In order to study the influence of the hydrogen concentration on the NO_x conversion and the ammonia selectivity, H₂ concentration in the rich pulses was varied between 1 and 6%. In addition, tests were performed with a higher catalyst amount (140 mg instead of 60mg previously) to ensure a possible complete hydrogen conversion.

Results obtained at 400°C are reported in Figure 2. Increasing the H₂ concentration from 1 to 2.5% leads to a significant enhancement of the NO_x conversion, from 28 to 77%. In this H₂ concentration range, H₂ is fully converted and nearly no ammonia is detected. Further increase of the H₂ concentration leads only to a small increase of the NO_x conversion. It varies from 83% to 87% when the H₂ concentration increases from 3% to 6%. In the same time, the ammonia selectivity continuously raises, it reaches 42% with 6% H₂ in the rich pulses. Finally, at 400°C, when the introduced H₂ is totally converted, the NO_x conversion is limited by the reducer amount, but the NO_x conversion is very selective in N₂. On the contrary, when residual hydrogen remains, ammonia selectivity dramatically increases even if the NO_x conversion is not total.

Figure 2: Pt/20Ba/Al catalyst (140mg): NOx storage/reduction efficiency test at 400°C. NOx conversion (%) into N₂ (□) and into NH₃ (■) and related data. Influence of H₂ concentration in the rich pulses (1-6%).

In order to obtain further information about the possible reactions occurring through the catalytic bed, tests with catalyst amounts of 60, 100 and 140 mg were performed with 2%, 3% and 6% H₂ in the rich pulses. Tests were done at 200, 300 and 400°C and the same trends were observed for the three studied temperatures. Results obtained at 400°C are reported in Figure 3. As expected, the NOx conversion increases when the catalyst amount increases whatever the concentration of hydrogen in the rich pulses. No crucial information is obtained with 6% H₂ in the rich pulses. The same behavior is obtained with the three tested catalyst masses: the selectivity of the reduction is rather similar and some hydrogen always remains. Whatever the catalyst mass, the same properties are observed along the catalytic bed. More interesting results are obtained with 2% H₂ in the rich pulses. The increase of the catalyst mass leads to both an enhancement of the NOx conversion and a decrease of the ammonia selectivity. In order to explain this result, the 140 mg catalytic bed can be divided into three parts which corresponds to the results obtained with 60, 100 and 140mg. Figure 3 indicates that ammonia and remaining hydrogen from the first 60mg catalytic bed react with the stored NOx on the end of the 100mg catalytic bed. Hydrogen is then nearly totally converted and a smaller ammonia amount is still available for the end of the 140mg catalytic bed. As no ammonia is observed at the outlet of the 140mg catalytic bed whereas the NOx conversion increases, it induces that ammonia can react with the stored NOx to form N₂.

An intermediary behavior is observed with 3% H₂ in the rich pulses. Increasing the catalyst mass from 60mg to 100mg leads to the same results as those obtained with 6% H₂: nitrogen and ammonia amounts increase at the reactor outlet and the introduced H₂ is not fully converted. Increasing the catalyst mass from 100mg to 140mg leads to similar results than those obtained

with 2% H₂: the NO_x conversion increases, the ammonia decreases and the introduced H₂ is nearly fully converted.

Then, the ammonia intermediate pathway is clearly putted in evidence for the reduction of the stored NO_x with H₂. When the introduced hydrogen is totally converted, the ammonia selectivity tends to be nil because the produced NH₃ can react with the remaining stored NO_x. In opposition, if the some hydrogen remains, the ammonia selectivity increases with the amount of excessive hydrogen. It induces that NO_x reduction with H₂ into ammonia is faster than the NO_x selective catalytic reduction with ammonia. This hypothesis is in accordance with the proposition of Lindholm et al. [39]. They have observed that during a long time rich period of several minutes, ammonia is not emitted at the beginning of the rich phase. They have suggested that the in situ produced ammonia firstly react with the stored NO_x. According to Cumaranatunge et al.[40], NH₃ is as efficient as H₂ for the NO_x reduction on Pt/Ba/Al₂O₃, which explain the delay for the NH₃ emission.

Figure 3: Pt/20Ba/Al catalyst: NO_x storage/reduction efficiency test at 400°C. NO_x conversion (%) into N₂ (□) and into NH₃ (■) and related data. Influence of H₂ concentration in the rich pulses (2, 3 and 6%) and influence of the catalyst mass (60, 100 and 140mg).

3.1.2.4. NO_x SCR with NH₃.

In order to confirm the catalyst activity for the NO_x SCR with ammonia, additional tests were performed. Two different SCR stoichiometries can be considered, depending on the presence of oxygen. The first one is observed in oxidizing mixture, with an excess of oxygen and corresponds to the following equations: $2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$ or $2\text{NH}_3 + 2\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$, known as fast and standard SCR, respectively. The second one corresponds to a stoichiometric mixture according the reaction $4\text{NH}_3 + 6\text{NO} \rightarrow 5\text{N}_2 + 6\text{H}_2\text{O}$, named slow SCR. Both conditions were tested between 150°C and 450°C using a 5°C min⁻¹ heating rate with simplified reaction mixtures: 500ppm NH₃, 500ppm NO and 2%O₂ balanced

in N_2 for the first considered stoichiometry, and 333ppm NH_3 and 500ppm NO balanced in N_2 for the slow SCR (m_{cata} : 60 mg ; total flow rate: $12L\ h^{-1}$).

Results obtained with the fast/standard SCR condition are reported in Figure 4a. This condition can be considered since the simultaneous presence of ammonia and oxygen is possible due to the mixing of the lean and rich mixtures. Reaction begins before $150^\circ C$ and the main product is N_2O . The maximum N_2O production is observed at $180^\circ C$, with a yield of 70%. The corresponding NO_x conversion reaches 80% and NH_3 is nearly totally converted. The N_2 yield, which is deduced from the N-balance reaches 20%. For temperatures higher than $210^\circ C$, competition with oxidation reaction appears. NH_3 is no more detected but NO and NO_2 concentration increase whereas N_2O and N_2 decrease. From this temperature, ammonia is predominantly oxidized into NO_x . These results are not in accordance with those obtained in cycling conditions, especially toward the N_2O emission. However, in cycling condition, NO_x reduction occurs during the rich pulses, i.e. in reducing atmosphere. As a consequence, a test was performed with the "slow SCR" condition, without oxygen. Results are reported in Figure 4b. NO and NH_3 conversion start near $180^\circ C$ and they are fully converted in N_2 for temperature higher than $220^\circ C$. N_2O is observed only near $200^\circ C$, with a maximum yield of 20%.

Thus, without oxygen in the feed stream, the NO SCR into N_2 only is obtained from $220^\circ C$ with the Pt/Ba/Al catalyst and using ammonia as reducer (light-off mode). This result confirms the previous hypothesis about the reaction of ammonia produced in-situ during the rich pulses and the stored NO_x to form N_2 .

Figure 4: NO_x SCR with NH_3 over Pt/20Ba/Al catalyst (60 mg). (a): fast/standard SCR light-off test with 500ppm NH_3 , 500ppm NO and 2% O_2 balanced in N_2 ; (b): slow SCR light-off test with 333ppm NH_3 and 500ppm NO in N_2 . Concentration of NH_3 (▪▪), NO_x (—), N_2O (··) and N_2 (—·).

3.1.3. Conclusion

The N_2 selectivity strongly depends on the hydrogen conversion introduced during the rich pulses. NH_3 is emitted since hydrogen is not fully converted, whatever the NO_x conversion rate. The ammonia selectivity increases with the hydrogen excess. Then, the ammonia pathway is clearly put in evidence. In addition, when H_2 remains in the reaction mixture, the ammonia production rate is higher than the ammonia reaction with NO_x in order to form N_2 .

3.2. Influence of Fe and Mn addition.

In a previous study [34], this kind of solids was already studied. However, many points are varying in this new work. For instance, barium and additive loadings are now two times higher and NO_x storage tests are performed using the same condition as the lean periods of the testing cycling condition.

The XRD characterization of Pt/20BaFe/Al (diffractograms not shown) shows that, in addition to $BaCO_3$ and $BaAl_2O_4$, characteristic diffraction peaks of Fe_2O_3 are also detected. No other phase including iron is detected. For Pt/20BaMn/Al, the $BaMnO_3$ phase was detected. In opposition with previous results obtained with lower Ba and Mn loading, Mn_2O_3 is also detected.

The storage capacities of the modified catalysts are compared with Pt20Ba/Al in Table 3. Whatever the temperature test, no significant influence of the additive is observed. Note that tests performed for 100s with lower barium and additive loadings showed that Mn and Fe addition slightly improved the NO_x storage capacity [34]. This observation clearly puts in evidence the crucial role of the storage kinetic in addition with the total storage capacity.

3.2.1. Influence of Fe addition on the NSR activity.

It was previously found that Pt/10FeBa/Al exhibited a lower NO_x conversion than Pt/10Ba/Al, [34]. Same results are obtained with Pt/20FeBa/Al. Even if neither the NO_x storage rate nor the NO oxidation rate (deduced from the NO_2/NO_x ratio at saturation) are modified by iron addition, the NO_x conversion decreases of about 30-40% depending on the temperature tests. It was proposed that some Pt-Fe interaction can occur [41], and decrease the platinum activity. Moreover, Luo et al. [42] have showed that iron addition in a Pt/Ba/ Al_2O_3 system decreases Pt-Ba interaction due to the platinum encapsulation in the Fe/FeOx lattice after repeated redox cycles for sulfur poisoning regeneration. Then, some repeatability tests in cycling condition were carried out with the iron modified catalyst. Successive tests were performed with the same sample. Note that before each test, the catalyst is submitted to a reducing treatment at 450°C for 15 min (rich mixture) in order to clean the catalyst surface, especially toward adsorbed NO_x . Figure 5 shows that the catalyst deactivation continue test after test, leading to a very low activity after four consecutive measurements. Then, the poisoning effect of iron addition is again put in evidence. Note that with the other catalysts tested in this study, there is no evolution of the catalyst activity during such consecutive tests.

Figure 5: Pt/20BaFe/Al catalyst (60mg): NOx storage/reduction efficiency test at 200, 300 and 400°C with 3% H₂ in the rich pulses. NOx conversion (%) into N₂ (■) and into NH₃ (■) and related data. Evolution of the catalyst behavior test after test (intermediate pretreatment: 450°C, 15 min under rich mixture).

3.2.2. Influence of Mn addition on the NSR activity.

3.2.2.1 Pt/20BaMn/Al catalyst (Mn/Ba molar ratio = 1).

NOx conversions obtained with the manganese modified catalyst are reported in Figure 6. For comparison, Pt/20Ba/Al is also reported. Two different trends are observed depending on the temperature test. At 200 and 300°C, catalyst with Mn exhibits lower NOx conversion and higher ammonia selectivity. On the contrary, test at 400°C showed a beneficial effect of Mn addition, with both a NOx conversion improvement from 45% to 62%, and a lower ammonia selectivity, from 31% to 7%. This low ammonia selectivity is associated with the total hydrogen consumption. It shows again the relation between the ammonia emission and the H₂ conversion. In order to have a better understanding of the role of manganese depending on the temperature test, a 20BaMn/Al sample without platinum was prepared using the same protocol as described in the experimental section, except for the platinum impregnation step which was simulated with an immersion in an ammonia solution. This sample was tested (i) alone and (ii) in association with Pt/20Ba/Al in two consecutive catalytic beds: 60mg of Pt/20Ba/Al and then 60mg of 20BaMn/Al. Catalytic tests results are reported in Figure 6. At 200 and 300°C, the activity of 20BaMn/Al tends to be nil. Then, as expected, results obtained with the association of Pt/20Ba/Al and 20BaMn/Al are similar with those obtained with Pt/20Ba/Al alone. It was also checked that same results are obtained with a mechanical mixture of both powders (results not shown). As described previously, Pt/20Ba/Al and Pt/20BaMn/Al catalysts exhibit similar NOx storage capacities. Then, the negative impact observed in NSR tests at 200°C and 300°C when manganese is added to the reference Pt/20Ba/Al sample is attributed to Pt-Mn interactions

which inhibit the reduction function of the catalyst. At 400°C, the activity of 20BaMn/Al became significant, with a NO_x conversion rate of 11% and an ammonia selectivity of 21%. This activity is attributed to manganese since a 20Ba/Al solid exhibits no DeNO_x activity (results not shown). Association of Pt/20Ba/Al and 20BaMn/Al leads to higher NO_x conversion compared with the addition of their own conversions, and also compared with Pt/20BaMn/Al. Then, platinum allows higher NO_x storage on 20BaMn/Al when placed before BaMn/Al. Concerning the role of Mn in the ammonia selectivity, comparison of Pt/20Ba/Al and Pt/20BaMn/Al indicates that in presence of Mn, a part of the produced ammonia react with stored NO_x, leading to both NO_x conversion improvement and ammonia selectivity decrease. Nevertheless, the hydrogen conversion is then total with Pt/20BaMn/Al, and it could play a crucial role on the ammonia selectivity, as previously discussed with Pt/20Ba/Al catalyst. Supplementary tests were then done with 6% H₂ in the rich pulses. In this case, H₂ was never fully converted. With Pt/20Ba/Al, the NO_x conversion, the ammonia selectivity and the hydrogen conversion are 48%, 43% and 63%, respectively. Addition of 20BaMn/Al in as a second catalytic bed led to values of 85%, 27% and 81%, respectively. Thus, even if hydrogen conversion is not total, manganese participates to the NO_x reduction with ammonia.

Figure 6: NO_x storage/reduction efficiency test at 200, 300 and 400°C with 3% H₂ in the rich pulses. NO_x conversion (%) into N₂ (□) and into NH₃ (■) and related data for Pt/20Ba/Al (60mg, noted Pt/Ba), Pt/20BaMn/Al (60mg, noted Pt/BaMn), 20BaMn/Al (60mg, noted BaMn), and association of both Pt/20Ba/Al (60mg) and 20BaMn/Al (60mg), (i) in two consecutive beds (noted Pt/Ba+BaMn) or (ii) mechanically mixed (noted Pt/Ba and BaMn).

Further investigations were done in order to study the influence the hydrogen concentration in the rich pulses on the behavior of Pt/20BaMn/Al catalyst. Results are reported in Figure 7. Until 3% H₂ in the rich pulses, NO_x conversion increases with hydrogen concentration and ammonia selectivity remains low, while the introduced hydrogen is fully converted. For higher hydrogen concentration, the NO_x conversion becomes near constant at around 70% but the ammonia selectivity significantly increases, and reaches 40% with 8% H₂. In fact, the same behavior was observed with 140mg of Pt/20Ba/Al. Figure 7 compares the results obtained with both catalysts using the same conditions ($m_{\text{cata}}=60\text{mg}$). For low hydrogen concentrations, NO_x conversions are similar but the NH₃ emission is significantly lower with the Mn modified catalyst, for which the introduced hydrogen is fully converted. For high hydrogen concentrations, H₂ remains at the reactor outlet for both catalysts and ammonia selectivity is always lower with the Mn modified catalyst even if it tends to be equivalent for the highest tested hydrogen concentrations. However, the NO_x conversion is approximately 40% higher with Pt/BaMn/Al. Then, the beneficial effect of the manganese addition for the NO_x reduction with the in-situ produced NH₃ is significant but the NO_x conversion is still limited.

Figure 7: 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 (60mg, ◆, ◇) and Pt/20BaMn/Al (60mg, ■, □).

3.2.2.2 Influence of the manganese loading

Finally, the influence of the manganese loading was studied. In addition to the Pt/20BaMn/Al catalyst previously studied (7.2wt% Mn, Mn/Ba molar ratio of 1), two other catalysts were prepared with Mn/Ba molar ratio of 0.5 and 1.5. They are noted Pt/20BaMn0.5/Al and Pt/20BaMn1.5/Al, respectively. The increase of the manganese content leads to a significant decrease of the specific surface area for Pt/20BaMn1.5/Al. It drops from 127 m²g⁻¹ for Pt/20Ba/Al, to 102 m²g⁻¹. The XRD analysis of the manganese containing catalysts shows that the intensities of the characteristic diffraction peaks of BaMnO₃ and Mn₂O₃ increase with Mn

loading (XRD patterns not shown). The H₂-TPR measurements in the 20-800°C temperature range (results not shown) indicate that the average oxidation degree increases from 3.2 for Pt/20BaMn0.5/Al to 3.7 pour Pt/20BaMn1.5/Al, assuming a Mn^{II} oxidation state at the end of the test. The increase of Mn^{IV} species with Mn loading was already showed on alumina by Kapteijn et all. [43]. For the studied Ba-Mn-Al catalysts, the formation of BaMnO₃ can also participate to the enhancement of Mn^{IV} species.

Concerning the NO_x storage capacity measured after 60s, there is no significant influence of the Mn loading. Similar NO₂/NO_x ratios were also observed after NO_x saturation, indicating similar behaviors for the NO into NO₂ oxidation reaction. NO_x removal efficiencies in cycling condition were measured and results are reported in Figure 8.

At 200 and 300°C, the inhibiting effect of the manganese addition is comparable whatever the manganese loading: The NO_x conversion decreases and the ammonia selectivity increases with Mn containing catalysts. Some differences appear at 400°C. Mn addition leads to an improvement of the NO_x conversion, an optimum of 62% is observed with Pt/BaMn/Al (Mn/Ba molar ratio = 1). For the higher Mn loading, the NO_x conversion decreases to 58%. It can be attributed to the loss of approximately 20% for the specific surface area. However, the ammonia selectivity continuously decreases with the manganese loading, at 18%, 7% and 5% for Pt/20BaMn0.5/Al, Pt/20BaMn/Al and Pt/20BaMn1.5/Al, respectively. Without manganese, the ammonia selectivity is 31%. These results show again the role of manganese on the NO_x reduction selectivity.

Figure 8: NO_x storage/reduction efficiency test at 200, 300 and 400°C with 3% H₂ in the rich pulses. NO_x conversion (%) into N₂ (□) and into NH₃ (■) and related data. Influence of manganese loading (expressed as Mn/Ba molar ratio) in Pt/20BaMnX/Al catalysts.

4. Conclusion

The NO_x reduction selectivity over Pt/Ba/Al catalyst tested in lean/rich cycling condition strongly depends on the hydrogen conversion introduced in the rich pulses. In fact, this catalyst is able to reduce NO_x into N₂ using NH₃ as reducer, but the ammonia formation rate via the NO_x reduction by H₂ is higher than the ammonia reaction rate with NO_x to form N₂. Then, NH₃ is emitted since hydrogen is not fully converted, whatever the NO_x conversion rate, and the ammonia selectivity increases with the hydrogen excess.

If H₂O and CO₂ both inhibit the NO_x storage, their roles differ for the NO_x reduction activity and selectivity. In accordance with the ammonia formation route via the isocyanate pathway, water inhibits the ammonia formation because it limits the formation of CO via the reverse WGS reaction, CO being necessary for isocyanate formation. CO₂ is known to favor the fast NO_x desorption during the rich pulses and to promote the hydrogen transformation into CO which is less efficient for the NO_x reduction. In addition, this CO formation also favors the ammonia formation via the isocyanate route.

Fe addition to Pt/20Ba/Al leads to a strong deactivation, probably due to interaction between iron and platinum, enhanced during the redox cycles.

Mn addition induces different behaviors depending on the temperature test. At low temperature (200-300°C), a significant decrease is observed, which is only attributed to the reducing step. Mn acts as a poison for the catalyst. In opposition, at 400°C, a significant enhancement of the NO_x conversion is observed after Mn addition. In the same time, the ammonia selectivity decreases. Thus, Mn favors the NO_x reduction with ammonia, even if the introduced hydrogen is not fully converted. However, when a large hydrogen excess is introduced, the ammonia selectivity tends to be similar with the one observed with Pt/20Ba/Al.

Finally, the NO_x conversion was largely improved at 400°C with manganese addition. However, the NO_x conversion at low temperature is still a problem and further investigations were done with Ce and Ce-Mn addition with interesting results. This study is detailed in part II of this work.

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