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A study of the ammonia selectivity on Pt/BaO/Al₂O₃ model catalyst during the NO_x storage and reduction process.

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Abstract:

The ammonia selectivity during the cycling NO_x storage reduction process over a model Pt/Ba/Al₂O₃ catalyst was studied. Firstly, it was demonstrated that, whereas the presence of water or carbon dioxide in the gas mixture have a negative effect on the storage step, the effect of these components have different impacts on the NO_x efficiency. Due to their involvement in the reverse water gas shift (RWGS) reaction, the absence of water in the gas mixture leads to a drop of the NO_x removal whereas without CO₂, an increase of the NO_x conversion is observed. It was also showed that the reducer (H₂) conversion during the short excursion in rich condition is directly correlated to the NH₃ emission. NH₃ is emitted since hydrogen is not fully converted, whatever the NO_x conversion rate. The ammonia pathway is clearly demonstrated and it was claim that, when H₂ remains in the reaction mixture, the ammonia production rate is higher than the ammonia reaction with the remaining NO_x in order to form N₂.

Key words: NO_x storage, NO_x reduction, ammonia, lean/rich cycles, barium.

1. Introduction

As a result of environmental legislations on the CO₂ emission from automotive source, the development of diesel and lean-burn engines is in perpetual growth since several years. Due to the presence of excess of oxygen in the exhaust gas, abatement of NO_x remains very difficult, and industrial or academic research groups are forced to propose new technological solutions. Thus, usually two main processes can be used to reduce NO_x in excess of oxygen. The first one is the Selective Catalytic Reduction (SCR) of NO_x. Numerous reducers have been investigated in the literature, such as hydrocarbons [1,2,3,4,5,6,7,8], oxygenated compounds [5,6,9,10] and nitrogen containing compounds (ammonia, urea, ...) [10,11,12,13,14]. The second possible solution is the use of the NO_x storage reduction (NSR) catalyst [15], working in transient periods: during the lean condition, NO_x are firstly oxidized and stored as nitrites or nitrates on a basic material, usually barium oxide. Periodically, the catalyst is regenerated: the stored NO_x are reduced in N₂ during a short excursion in rich condition. Nevertheless the major drawback of this system is the deactivation of the catalyst, mainly due to sulfur poisoning [16,17], and the thermal aging [18,19]. It was also reported that ammonia emission can be formed during the short excursion under rich conditions, especially when hydrogen is used as reducer [20,21,22,23,24,25]. In the literature, it was suspected that the NH₃ production should be correlated to the barium loading [26], the temperature reaction [27,28,29] or the reducer concentration [30,31].

However, some points are still in opposition, and the objective of this work 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 [32].

2. Experimental Part

2.1. Catalysts preparation

The reference catalyst contains 1wt% Pt and 20wt% BaO on alumina. 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. The Ba(NO₃)₂ salt was 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 $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ aqueous solution. After drying, the catalyst was pre-treated at 700°C for 4h under N_2 , in order to stabilize Pt and Ba before the final hydrothermal treatment at 700°C for 4h (10% O_2 , 5% H_2O in N_2) [33]. The obtained catalysts are noted Pt/20Ba/Al and exhibits BET specific surface areas of $127 \text{ m}^2\text{g}^{-1}$.

2.2. Specific surface measurement

The BET surface areas were deduced from N_2 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 in order to eliminate the adsorbed species.

2.3. XRD analysis

X-ray powder diffraction was performed at room temperature with a Bruker D5005 using a $\text{K}\alpha$ 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.

2.4. NO_x storage capacity (NSC) measurement

Before each measurement, the catalyst (60mg) was pretreated in situ for 30 min at 550°C , under a 10% O_2 , 10% H_2O , 10% CO_2 and N_2 mixture (total flow rate: $10 \text{ L}\cdot\text{h}^{-1}$), 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 H_2O which was introduced using a saturator. Both NO and NO_x concentrations ($\text{NO}+\text{NO}_2$) were followed by chemiluminescence. H_2O 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. In addition, the platinum oxidation activity was estimated as the NO_2/NO_x ratio (%) at saturation (usually after about 900s).

Table 1: Rich and lean gas compositions used for the NO_x conversion test (60s lean / 3s rich). Total flow rate: 10 L h^{-1} .

Gas	NO	H ₂	O ₂	CO ₂	H ₂ O	N ₂
Rich	-	1 to 9%	-	10%	10%	Balance
Lean	500ppm	-	10%	10%	10%	Balance

2.5. NO_x conversion in cycling conditions

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. Hydrogen concentration in the rich pulse is usually 3%, but additional tests were performed with variable contents in hydrogen (1% to 9%).

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 30 minutes in a dry condenser and then analyzed by two different HPLC for NH₄⁺, NO₂⁻ and NO₃⁻. NO₂⁻ and NO₃⁻ were added to the unconverted NO_x. The N₂ selectivity is calculated assuming no other N-compounds than NO, NO₂, N₂O and NH₃. Some tests were also performed using a Multigas FTIR detector (MKS 2030) without water trap system and same results were then obtained.

3. Results and discussion

The X ray diffractograms obtained with reference Pt/20Ba/Al before and after the platinum impregnation step were previously studied in [32,34]. It was demonstrated that the main crystallized phases detected are BaCO₃ and BaAl₂O₄. Some phase transformation occurred during the platinum addition. The XRD pattern of the 20Ba/Al support powder exhibits significantly more intense BaCO₃ and BaAl₂O₄ diffraction peaks than for the platinum supported Pt/20Ba/Al catalyst. It can be attributed to barium leaching from the support during the platinum impregnation step [35,36].

3.1 Effect of water and carbon dioxide on the NO_x storage-reduction (NSR) process

During the first step of NO_x storage reduction (NSR) process, NO_x are stored on basic sites of the support. In order to understand the role of water and carbon dioxide on the whole NSR process, their influences were firstly investigated on the NO_x storage step. The effect of water is studied in the presence of CO₂ and the effect of CO₂ is studied in the presence of H₂O.

3.1.1 NO_x storage measurements

Figure 1 displays the effect of water and carbon dioxide on the NO_x storage rate for 60s for the Pt/20Ba/Al model catalyst. The NO oxidation activity is assessed using the NO₂/NO_x ratio measured after saturation (commonly after 900s). Firstly, with H₂O and CO₂ in the gas mixture, it appears that the NO_x storage capacity increases versus temperature, from 57% at 200°C until 83% at 400°C. Then, whatever the temperature test, the inlet NO_x are not totally stored in 60s. With the complete gas mixture, results reported in Figure 1 show that NO₂/NO_x ratio is about 9% at 200°C and increases continually with temperature to reach 42% at 400°C.

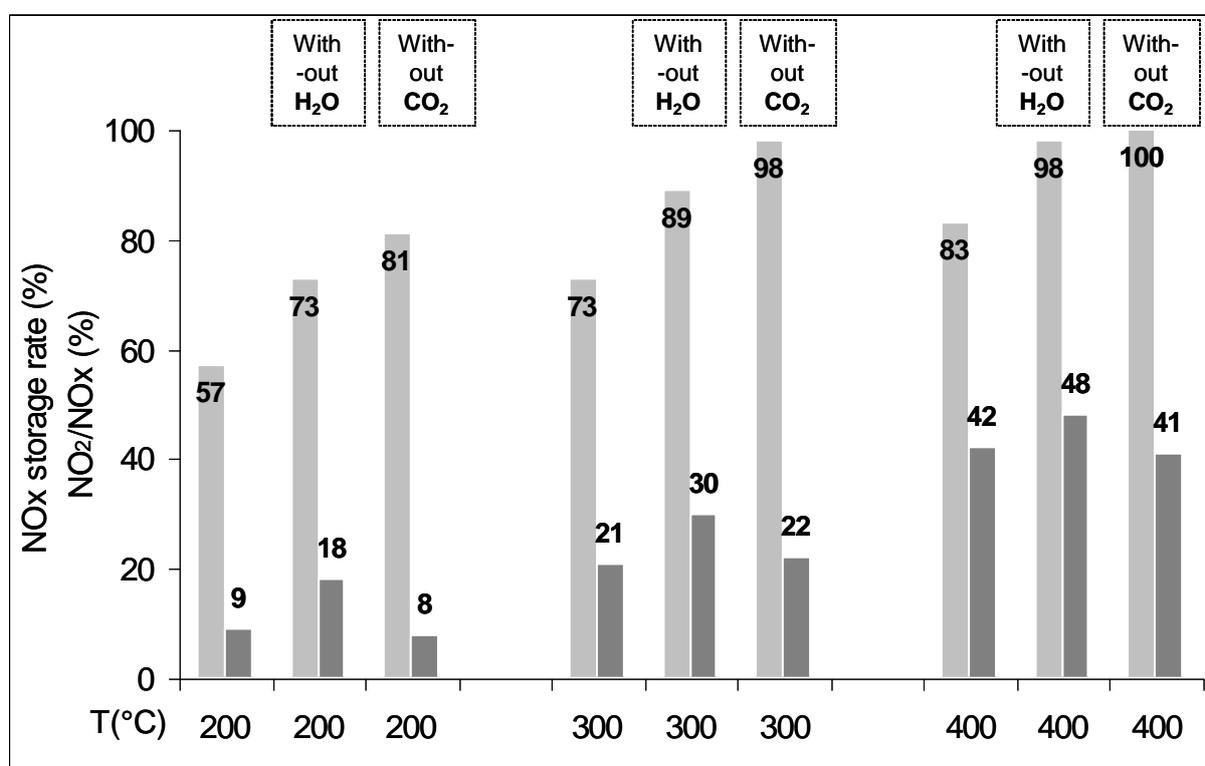


Figure 1: NO_x storage rate (■) and NO₂/NO_x ratio (■) versus temperature toward Pt/20Ba/Al model catalyst.

In order to study the influence of water, some tests were performed without H₂O in the reaction mixture. Tests without water lead to significant enhancements of the NO_x storage capacities, from 73% at 200°C, to a total stored NO_x at 400°C (98%, Figure 1). As previously observed [32], this can be attributed to the inhibiting effect of water on the NO to NO₂ oxidation rate. 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. When H₂O is removed, they reach 18%, 30% and 48%, respectively.

When CO₂ is removed from the feed gas, the NO_x storage capacities also increase. Near all the introduced NO_x are trapped at 300 and 400°C (Figure 1). In another words, the inhibiting effect of CO₂ is stronger compared with the H₂O inhibiting effect. In opposition with H₂O, CO₂ has no influence on the NO to NO₂ oxidation rate since the NO₂/NO_x ratios at saturation remain unchanged when CO₂ is removed from the reaction mixture. The inhibiting effect of CO₂ on the NO_x storage was attributed to the competition between nitrates and carbonates formation on the storage sites [32].

3.1.2 NO_x storage-reduction (NSR) efficiency

Results on the influence of water and carbon dioxide on the NO_x storage-reduction efficiency were reported on Figure 2. The H₂ concentration in the rich pulse is 3% (duration: 3s).

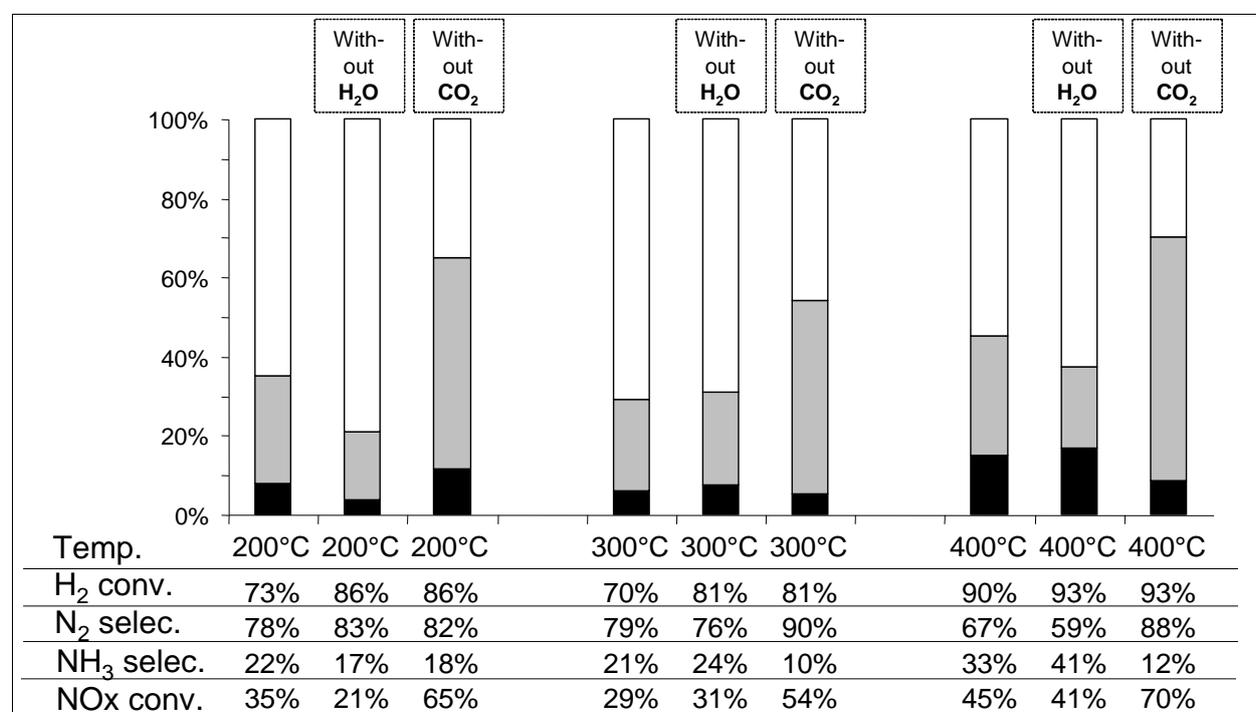


Figure 2: Pt/20Ba/Al catalyst (60 mg): NO_x storage/reduction efficiency test at 200, 300 and 400°C with 3% H₂ in the rich pulses. NO_x conversion (%) into N₂ (□) and into NH₃ (■) and related data. Influence of CO₂ and H₂O.

First, note that N₂O was never significantly observed during these tests in cycling condition, whatever the temperature test. This point is consistent with the study of Abdulhamidet al. [24] who claims that N₂O is mainly obtained with CO as reducer. Besides, whatever the tested temperatures, comparison of Figure 1 and Figure 2 shows that the NO_x reduction efficiency is always lower than the NO_x storage rate, showing that the limiting step of this process is the

reduction phase. This observation is confirmed by the fact that the introduced hydrogen is not fully converted, whatever the temperature. Using the complete mixture, including H₂O and CO₂, 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°C and 300°C and 33% at 400°C.

In opposition with the storage tests, NO_x storage/reduction tests in absence of water, leads to a deterioration in the reduction rate, especially at 200°C. This can be attributed to the reverse water gas shift reaction (RWGS, $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$) which is favored in absence of water, and lead to the production of CO, confirmed by the measurement of 350 ppm (detected at the outlet with a Multigas FTIR analyzer, MKS 2030). Since H₂ is reported to be more active than CO for NO_x reduction at low temperature [15], it explains results reported in Figure 2. Besides, note that, while NO_x conversion is lower without H₂O, the H₂ conversion increases (Figure 2), showing that the reducer also react with CO₂, according to the RWGS reaction. Moreover, the reverse water gas shift reaction can also explain the higher ammonia selectivity in absence of water observed at 300 and 400°C. Indeed, Lesage et al. [37,38] have proposed that the NH₃ formation come from the isocyanate hydrolysis ($2 \text{NCO} + 3 \text{H}_2\text{O} \rightleftharpoons 2 \text{NH}_3 + 2 \text{CO}_2 + \frac{1}{2} \text{O}_2$) when CO is present during the rich periods. Besides, even if H₂O is not present in the gas mixture, it is not the limiting reactant for the isocyanate hydrolysis reaction since the converted hydrogen is mainly oxidized in H₂O.

It was previously reported in Figure 1 that CO₂ inhibits the NO_x storage, with a drop around 20%-30%. During the NO_x storage/reduction test in cycling condition, CO₂ leads to a higher loss between 35% and 45%. 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 [39], leading to higher NO_x slip. Furthermore, with CO₂ in the feed stream, the reverse water gas shift reaction ($\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$) is favored. H₂ is partially converted into CO which is less active than hydrogen for the NO_x reduction [15]. Another interesting point is the relatively low ammonia selectivity when CO₂ is removed from the feed stream. In fact, without CO₂, the CO formation (via the RWGS reaction) is not possible. As a consequence, formation of isocyanate, which is considered as ammonia precursor [37,38], is unexpected. However, NH₃ is detected at a lower level even if there is no carbon source in the used reaction mixture. It induces that the isocyanate hydrolysis is not the only way to obtain ammonia.

To conclude, water and carbon dioxide have an important impact in the RWGS reaction. In absence of water in the gas mixture, the production of CO is enhanced, leading to a drop of the

NO_x reduction and an increase of the ammonia production at high temperature. These results are explained by the fact that CO has been advanced as a precursor of intermediates isocyanates species, involved in the ammonia reaction pathway. A similar trend is observed with CO₂. In fact in absence of carbon dioxide, the CO formation is not possible, and the ammonia yield consistently decreases.

3.2 Effect of hydrogen concentration on the NSR efficiency

Effect of H₂ concentration (from 1% up to 9%) on the NSR efficiency at 400°C was reported on Table 2. Results were obtained with both H₂O and CO₂ in the feed stream.

First, with 60mg of catalyst, it appears from results display on Table 2, that the increase of the H₂ concentration leads to only a small increase of the NO_x conversion, from 37% with 1% H₂ to 49% with 9% H₂. In parallel, a significant increase of the NH₃ selectivity is measured with the increase of the H₂ conversion, showing that the higher the hydrogen consumed, the lower the NH₃ produced. However, whatever the H₂ concentration in the inlet gas, hydrogen was never fully converted. In order to study the catalyst behavior at higher hydrogen consumption, some supplementary tests were performed with higher catalyst weight. Results are reported on Table 3 and Figure 3.

The evolution of NO_x conversion as well as the nitrogen selectivity versus the amount of hydrogen in the rich pulse is presented in Figure 3. It appears that the increases of the hydrogen concentration lead to a significant enhancement the NO_x conversion, especially when H₂ concentration varies between 1% and 2.5% in the rich pulses. In a same time, on this hydrogen range, no ammonia emission is observed, and H₂ is fully converted (Table 3).

Table 2: Effect of H₂ concentration on the NSR efficiency at 400°C with 60mg of the Pt/20Ba/Al catalyst.

H ₂ inlet in the rich pulses (%)	1	1.5	2	3	4	5	6	9
H ₂ conv. (%)	99	95	88	85	69	61	63	55
S _{N2} (%)	87	80	67	67	60	57	57	53
S _{NH3} (%)	13	20	33	33	40	43	43	47
NO _x conv. (%)	37	41	44	45	44	45	48	49

Table 3: Effect of H₂ concentration on the NSR efficiency at 400°C with 140mg of the Pt/20Ba/Al catalyst.

H ₂ inlet	1	1.5	2	2.5	3	3.5	4	4.5	5	6
in the rich pulses (%)										
H ₂ conv. (%)	100	100	100	100	99	97	90	88	84	79
S _{N2} (%)	100	100	100	97	83	73	70	66	61	58
S _{NH3} (%)	0	0	0	3	17	27	30	34	39	42
NO _x conv. (%)	28	44	62	77	83	84	86	86	86	87

Table 4: Effect of the Pt/20Ba/Al catalyst weight at 400°C on the NSR efficiency for 2%, 3% and 6% of hydrogen in the rich pulse.

H ₂ inlet	2%		
Catalyst weight (mg)	60	100	140
H ₂ conv. (%)	88	99	100
S _{N2} (%)	67	85	100
S _{NH3} (%)	33	15	0
NO _x conv. (%)	44	52	62

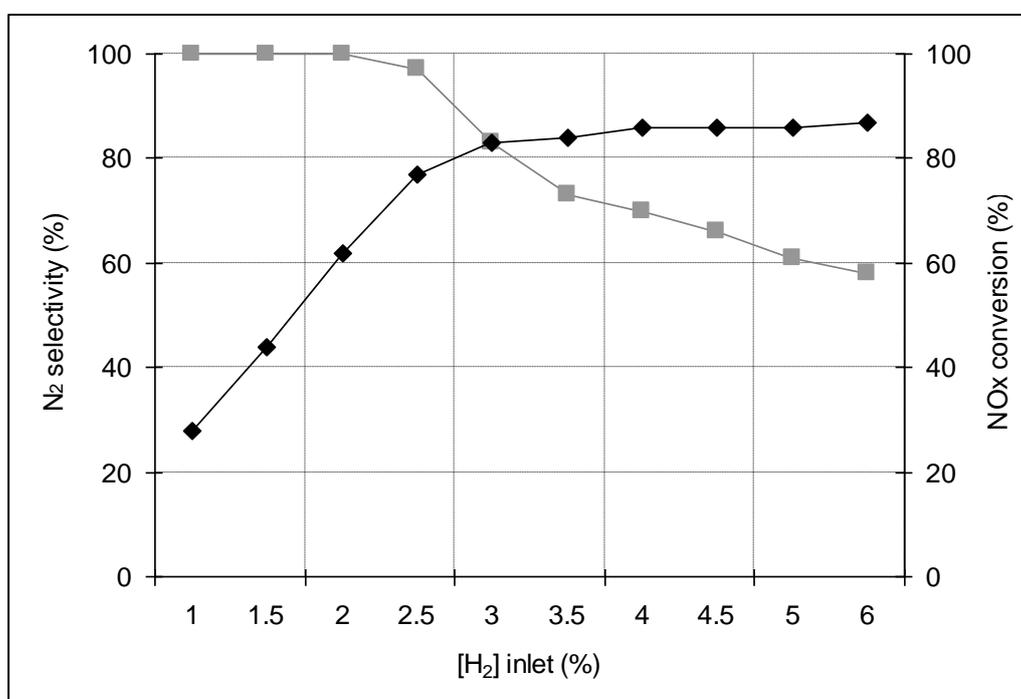


Figure 3: Nitrogen selectivity (■) and NO_x conversion (◆) versus the amount of hydrogen in the rich pulse with 140mg of Pt/20Ba/Al catalyst at 400°C.

For higher H₂ concentration (3% to 6%), NO_x conversion varies only between 83% and 87%. In parallel, NH₃ selectivity strongly increases from 17% to 42%, and hydrogen is then not fully converted.

To conclude, the fact that NO_x conversion increases, whereas H₂ is fully converted and that no ammonia emission was observed, suggests a NO_x reduction by NH₃ as reducer. This assumption was examined assuming three parts in the catalytic bed: 60mg, 100mg and 140mg. Catalytic tests were performed with 2%, 3% and 6% of hydrogen in the rich pulses and only results with 2% of H₂ at 400°C are presented in Table 4. It was observed that, when catalyst weight increases, H₂ conversion increases. In parallel, NH₃ selectivity decreases until no ammonia emission was detected when H₂ is fully converted. In the same time NO_x conversion is enhanced.

4. Discussion

From the results presented below, ammonia intermediate pathway was clearly demonstrated for the reduction of the stored NO_x with H₂. It appears that, when hydrogen is missing in the rich pulses, that is fully converted, the ammonia selectivity tends to be nil because the produced NH₃ can react with the remaining stored NO_x. In opposition, if 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. [40]. 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 Cumararatunge et al. [41], NH₃ is as efficient as H₂ for the NO_x reduction on Pt/Ba/Al₂O₃, which explain the delay for the NH₃ emission.

In order to check the catalyst activity for the NO_x SCR with ammonia, additional tests were performed. In the literature, fast and slow NH₃-SCR reaction can be considered, respectively in oxidizing or in stoichiometric condition. The last condition seems more auspicious to the NSR results presented below (i.e, without oxygen in the rich pulse). Thus, the slow SCR corresponds to stoichiometric mixture according the reaction $4\text{NH}_3 + 6\text{NO} \rightarrow 5\text{N}_2 + 6\text{H}_2\text{O}$. This condition was tested between 150°C and 450°C using a 5°C min⁻¹ heating rate with simplified reaction mixtures: 333ppm NH₃ and 500ppm NO balanced in N₂ (m_{cata}: 60 mg ; total flow rate: 12L h⁻¹, results not shown). It was evidenced that NO and NH₃ conversion start near 180°C and they are

fully converted in N_2 for temperature higher than 220°C . N_2O is observed only near 200°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°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 .

5. Conclusion

Pt/20Ba/Al catalyst was used as a reference material for the study of the NO_x storage-reduction process. Effect of water and carbon dioxide toward the NO_x efficiency was measured at 200°C , 300°C and 400°C , and compared with the NO_x storage properties of the sample. Finally, H_2O and CO_2 both inhibit the NO_x storage, because of NO oxidation inhibition and carbonate/nitrate competition, respectively. Concerning the reduction step, water induces a positive effect by limiting the hydrogen transformation into CO via the reverse WGS. On the contrary, CO_2 favors the fast NO_x desorption during the rich pulses 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.

A special attention was then carried out on the ammonia emission of the reduction step. It was clearly demonstrated that 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 .

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