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Influence of Mn and Fe addition on the NO_x storage-reduction properties and SO₂ poisoning of a Pt/Ba/Al₂O₃ model catalyst.

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Abstract

This work deals with the effect of Mn or Fe addition on the NO_x storage-reduction properties of a Pt/Ba/Al₂O₃ model catalyst. NO_x storage capacity, SO₂ poisoning and regeneration and NO_x removal efficiency under rich/lean cycling conditions are studied.

Fe addition to Pt/Ba/Al₂O₃ leads only to a small increase of NO_x storage capacity, and more interestingly, to a better sulfur removal due to the inhibition of bulk barium sulfate formation. Unfortunately, the NO_x storage property cannot be fully recovered. Moreover, Fe addition results in a decrease in the NO_x removal efficiency. Mn addition also improves the NO_x storage capacity, but no significant influence on the sulfur elimination is observed. Mn-doped catalyst does not improve the NO_x removal efficiency, but NH₃ selectivity is found to drastically decrease at 400°C, from 20% to 3%. In addition, the NO_x conversion can be improved at higher H₂ concentration in the rich pulse, always keeping NH₃ selectivity at low level.

Keywords: NO_x, storage, reduction, SO₂ poisoning, Pt, Ba, Fe, Mn.

Introduction

The NO_x storage reduction (NSR) process is presented as a possible solution to reduce NO_x emissions from lean burn engine. A drawback to this system is the catalyst deactivation, mainly due to (i) sulfur poisoning [1,2] even if the sulfur content in fuels is lowered and (ii) thermal aging [3]. 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 [4,5].

The impact of the support oxide on the NO_x storage properties of Pt–Ba catalysts, especially toward sulfur resistance and sulfur regeneration, was studied in previous works [6,7]. The aim of this work is to determine the effect of Mn and Fe addition on the properties of a Pt/Ba/Al₂O₃ model catalyst. Mn is known to be active in NO oxidation, a crucial step for the storage process [8,9]. Moreover, Mn can also participate to the NO_x storage [10,11] and presents an activity in the NO_x reduction by NH₃ reaction [12,13]. Fe is generally added in NSR formulations to improve the catalyst sulfur resistance. Iron oxide is reported to inhibit the bulk barium sulfates formation [14,15].

In addition to the NO_x storage capacity measurements and the sulfur impact evaluation, the NO_x removal efficiency of the studied catalysts was measured under cycling conditions. Activity and selectivity, especially toward NH₃ emission, are considered.

Experimental

The reference catalyst contains 1wt% Pt and 10wt% BaO on alumina. In addition, the modified samples contain 3.8wt% Mn or 3.9wt% Fe, corresponding to a Ba/additive 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 [16], the intermediate nitrogen treatment allows a higher platinum-barium dispersion. The obtained catalysts, named stabilized, are noted Pt/10Ba/Al, Pt/10BaMn/Al and Pt/10BaFe/Al. They exhibit BET specific surface areas of 172 m².g⁻¹, 150 m².g⁻¹ and 151 m².g⁻¹, respectively.

X-ray powder diffraction was performed at room temperature using a Bruker D5005 diffractometer equipped with a K α Cu radiation (λ =1.54056 Å).

NO_x storage capacities were measured at 300°C under dynamic conditions with a mixture containing 350ppm NO, 10% O₂, 10% CO₂ and 10% H₂O in N₂ (GHSV=100000 h⁻¹). The NO_x storage capacity was estimated by the integration of the recorded profile after subtraction of the contribution of the apparatus (dead volume) deduced from a test without catalyst. The reported data correspond to 100s of storage. In this case, 67 μ mol NO_x per gram of catalyst passed through the catalyst. The sulfating treatment was performed at 300°C with SO₂ and corresponds to a 2.0 wt% S theoretical content if all the sulfur is stored on the catalyst. The regeneration of sulfated catalysts was carried out at 550°C for 30 min under rich conditions with a mixture containing 2.5% H₂, 10% CO₂, and 10% H₂O in N₂.

Sulfates stability was evaluated by H₂-TPR. The sample was first in-situ pretreated at 300°C under pure oxygen. The reduction was carried out with 1% H₂ from room temperature up to 800°C.

NO_x removal efficiency was measured over stabilized catalysts under cycling conditions (60s lean / 3s rich) at 200, 300 and 400°C. The lean and rich reaction mixtures are described in Table 1. NO and NO_x concentrations (NO+NO₂) were followed by chemiluminescence, N₂O by FT-IR and H₂ using a mass spectrometer. For each tested temperature, water was condensed at 0°C at the reactor outlet and before the analyzers, during 30 min for each temperature after signals stabilization. The ammonia and the nitrate/nitrite amounts trapped in the condensed water were analyzed using two HPLC. Some tests were also performed using a multigas FT-IR detector (MKS 2030).

Table1: Rich and lean gas compositions used for the NO_x conversion test (60s lean / 3s rich). GHSV=100000 h⁻¹

Gas	NO	H ₂	O ₂	CO ₂	H ₂ O	N ₂
Rich	-	3, 6 or 9%	0.02%	10%	10%	Balance
Lean	500ppm	-	10%	10%	10%	Balance

Results and discussion

Characterization of the stabilized catalysts.

The three samples were characterized by X-ray diffraction before and after platinum impregnation (diffractograms not shown). The BaAl₂O₄ structure is detected in all samples but at higher intensity before platinum impregnation and consecutive calcination. Indeed, BaAl₂O₄ is partially soluble in the platinum impregnation solution and it was not fully reformed, even after the two final thermal treatments at 700°C. In opposition, BaCO₃ is clearly identified after stabilization of the catalysts whereas this structure was not evidenced before the platinum impregnation.. In addition to BaCO₃ and BaAl₂O₄, weak reflections attributed to Fe₂O₃ are observed in Pt/10BaFe/Al. For Pt/10BaMn/Al, the BaMnO₃ phase was detected before the platinum impregnation, but the diffraction peaks nearly disappeared in the stabilized catalyst. No other manganese oxide phase have been detected whatever the preparation step.

H₂-TPR profiles of the stabilized catalysts are reported in Figure 1. No significant H₂ consumption is observed in the 100-800°C temperature range for the Pt/10Ba/Al catalyst. Addition of Mn induces a main reduction peak around 300°C. This peak is assigned to the reduction of manganese oxides into MnO. According to Laberty et al. [17], the reduction of MnO₂ into MnO occurs between 250 and 450°C, with intermediate formation of the Mn₂O₃ and Mn₃O₄ phases. Taking into account the H₂ consumption in the 100-800°C temperature range, a mean oxidation state of 3.22 is calculated for Mn, indicating mainly the presence of Mn^{III} (for instance Mn₂O₃) and Mn^{IV} (*i.e.* BaMnO₃ as detected by XRD, and/or MnO₂) before reduction.

The iron oxide reduction occurs at high temperature, with a broad reduction peak between 450 and 800°C. Tang et al. [18] have established that Fe₂O₃ is firstly reduced into Fe₃O₄ between 300 and 470°C and formation of Fe^{II}/Fe^{III}-based aluminates are observed. Reduction of the aluminates occurs from 500 to 1000°C. Then, iron in Pt/10Fe/Al should mainly exist as aluminates, even if no corresponding XRD peaks were observed. Assuming

a Fe^{III} into Fe° reduction, the H_2 consumption in the 100-800°C temperature range would correspond to a reduction rate in metallic iron of 57%. It means that iron is not fully reduced, and should partially remains as hardly reducible aluminate species.

NO_x storage capacity, SO₂ poisoning and regeneration.

The storage capacities of the stabilized catalysts, measured at 300°C, are reported in Table 2. Mn and Fe addition is found to slightly improve the NO_x storage capacity. Pt/10BaMn/Al exhibits the higher value, with 39.5 $\mu\text{mol.g}^{-1}$, versus 35.8 $\mu\text{mol.g}^{-1}$ and 31.2 $\mu\text{mol.g}^{-1}$ for Pt/10BaFe/Al and Pt/Ba/Al, respectively. In order to clarify the role of Fe and Mn, additional tests were performed at 300°C without H_2O and CO_2 in the reaction mixture. Compared to Pt/Ba/Al, the storage capacity at saturation (after 900 s) was 15% higher after Mn addition, indicating an increase in the storage sites number, but no improvement of the NO oxidation rate was observed (NO_2/NO_x molar ratio after saturation close to 25%). However, a 10BaMn/Al sample without platinum is able to store NO_x (75% of the capacity obtained at 100s with Pt/10BaMn/Al), with a NO_2/NO_x ratio at saturation of 20%. Then, Mn may participate to the NO oxidation and to the NO_x storage as mentioned by Bentrup et al. [10] and Xiao et al. [11].

Iron addition does not modify the total number of available sites for the NO_x storage, estimated at saturation without H_2O and CO_2 in the feed stream, in accordance with the results of Yamakasi et al. [12]. The improvement of the NO_x storage capacity at 100s with H_2O and CO_2 in the feed stream could be attributed to a decrease of the catalyst basicity. Indeed, Pt/10BaFe/Al is less sensitive to H_2O and CO_2 than Pt/10Ba/Al, the loss of storage capacity being 16% and 27%, respectively. This suggests a lower adsorption competition between NO_x and CO_2 (mainly) when Fe is added to the Pt/10Ba/Al catalyst, which is typical of a basicity decrease [19].

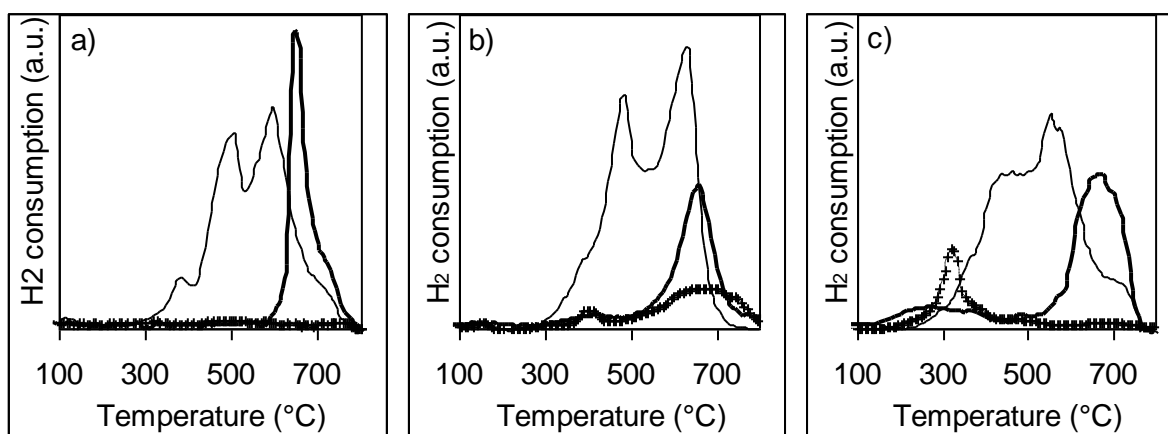


Figure 1: TPR profile of a) Pt/10Ba/Al, b) Pt/10BaFe/Al and c) Pt/10BaMn/A).
(++) stabilized catalysts, (-) sulfated catalysts; (-) regenerated catalysts.

Table 2: NO_x storage capacity (NSC) measured at 100s at 300°C (μmol.g⁻¹); impact of the sulfur poisoning

<i>Catalyst</i>	<i>Pt/10Ba/Al</i>	<i>Pt/10BaFe/Al</i>	<i>Pt/10BaMn/Al</i>
Stabilized	31.2	35.8	39.5
Sulfated (Deposited sulfur wt%)	13.2 (1.7%S)	20.3 (1.8%S)	24.6 (1.7%S)
Regenerated at 550°C (S elimination rate)	29.7 (58%)	28.0 (80%)	33.8 (50%)
NSC recovery (%)	95%	78%	86%

After the sulfating treatment, the NO_x storage capacities strongly decrease (Table 2). For Pt/10Ba/Al, a loss of 48% is observed. Fe and Mn doped samples are more resistant toward the poisoning treatment, with a loss of only 30%. Thus, the obtained NO_x storage capacities are significantly higher, between 20.3 and 24.6 μmol.g⁻¹ versus 13.2 μmol.g⁻¹ for Pt/10Ba/Al. The sulfated catalysts were characterized by H₂-TPR (Figure 1). As previously described [7], the TPR profile of the sulfated Pt/10Ba/Al catalyst exhibits two main peaks around 500 and 600°C. The first one is attributed to the simultaneous reduction of aluminum sulfates and some well dispersed barium sulfates located in platinum proximity. The second peak, around 600°C, is ascribed to the reduction of surface barium sulfates, and the observed shoulder near 750°C corresponds to bulk barium sulfate reduction.

Addition of Mn or Fe does not strongly modify the sulfates stabilities. The more interesting point is that Pt/10BaFe/Al exhibits a reduction ending below 700°C while 750°C is needed for the two other samples. This is attributed to a limitation of bulk barium sulfate formation in the Fe-doped catalyst, as previously mentioned [12-13]. Then, even if X-ray diffraction does not evidence the presence of Ba-Fe mixed-oxide species, interactions between these two compounds cannot be excluded. Assuming a H₂/SO₄²⁻ ratio of 4 for the sulfate reduction ($X-SO_4 + 4H_2 \rightarrow X-S + 4H_2O$ and/or $X-SO_4 + 4H_2 \rightarrow X-O + H_2S + 3H_2O$), a total sulfur content of about 1.7 wt% was deduced from hydrogen consumption whatever the catalyst, after subtraction of the contribution of the Mn and Fe oxides reduction (Table 2).

The catalysts were also characterized by H₂-TPR after the sulfur regeneration treatment (Figure 1). For Pt/10Ba/Al, the H₂ consumption indicates that 58% of the deposited sulfur is removed, but a stabilization of the remaining sulfates is observed. Similar result is observed with Pt/10BaMn/Al, with 50% sulfur elimination and stabilization of the remaining sulfates. As expected, the sulfur removal is improved over Pt/10BaFe/Al since 80% of the initially deposited sulfur is eliminated after the regeneration procedure. This is in accordance with a weaker sulfate stability, with nearly no bulk sulfate formation.

Concerning the NO_x storage capacities, 95% of the initial value is recovered over Pt/10Ba/Al (Table 2), indicating an efficient regeneration of the NO_x storage sites. This rate decreases to 86% and to only 78% for Pt/10BaMn/Al and Pt/10Fe/Al, respectively. Then, the Fe-doped catalyst exhibits the lower NO_x storage capacity after regeneration (28.0 μmol.g⁻¹, Table 2). In addition to a possible incomplete surface cleaning, the reducing treatment can induce some structural changes in the doped catalysts. Indeed, a slight deactivation of the Pt/10BaMn/Al catalyst was also observed after the sulfur regeneration treatment without previous sulfating procedure. The H₂-TPR experiment (not shown) indicates a lower mean oxidation degree for Mn, even after re-oxidation at 550°C.

Consequently, high Mn oxidation state is needed to improve the NO_x storage properties. For the iron modified catalyst, some Pt-Fe interaction can occur [20], and decrease the platinum activity.

NO_x removal efficiency.

The NO_x removal efficiencies measured under lean/rich cycling conditions are reported in Table 3. Typical recorded curves, obtained with Pt/10Ba/Al at 400°C, are presented in Figure 2. Whatever the catalyst and the test temperature, no significant amount of N₂O was measured. For all the catalysts, the NO_x conversion as well as the H₂ consumption rate increase with temperature. With 3% H₂ in the rich mixture, the H₂ conversion is found to increase from 84-88% at 200°C to 98-100% at 400°C.

For Pt/10Ba/Al, the NO_x conversion varies from 20% at 200°C to 46% at 400°C. The NH₃ selectivity remains around 20%, whatever the reaction temperature. Pt/10FeBa/Al exhibits a lower NO_x removal efficiency, especially at 300 and 400°C with only 21% and 33%, respectively. Compared to Pt/10Ba/Al, the NO_x conversion is not strongly affected by the Mn addition, even if slightly lower conversions are obtained at 300 and 400°C. The most interesting point is that the Mn adding results in a dramatically decrease in the NH₃ selectivity to only 3% at 400°C, while H₂ conversion is complete. In order to verify if the NO_x removal efficiency can be improved with this catalyst, always keeping the ammonia selectivity a low value, additional tests were performed at 400°C by increasing the H₂ concentration in the rich pulse. Increasing the H₂ concentration up to 6% leads to an almost total NO_x conversion, and N₂ selectivity still reaches 99% (Table 3). Note that the H₂ consumption is still 100%. Increasing the H₂ concentration up to 9% leads only to a slightly higher NH₃ selectivity (7%), and H₂ is no more totally converted.

These results clearly indicate that the NO_x reduction to N₂ is strongly promoted at 400°C by Mn addition. A significant improvement of the NO_x reduction by NH₃, produced in-situ in the course of the rich pulse, is suggested to be responsible of the high N₂ selectivity observed over the Mn-doped catalyst. Finally, 6% H₂ is the optimal concentration with our test conditions between the ammonia formation rate and the quantity of stored NO_x. Indeed, a higher H₂ concentration induces a too high ammonia formation rate toward the stored NO_x, a NH₃/NO_x=1 ratio being optimal assuming $2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$.

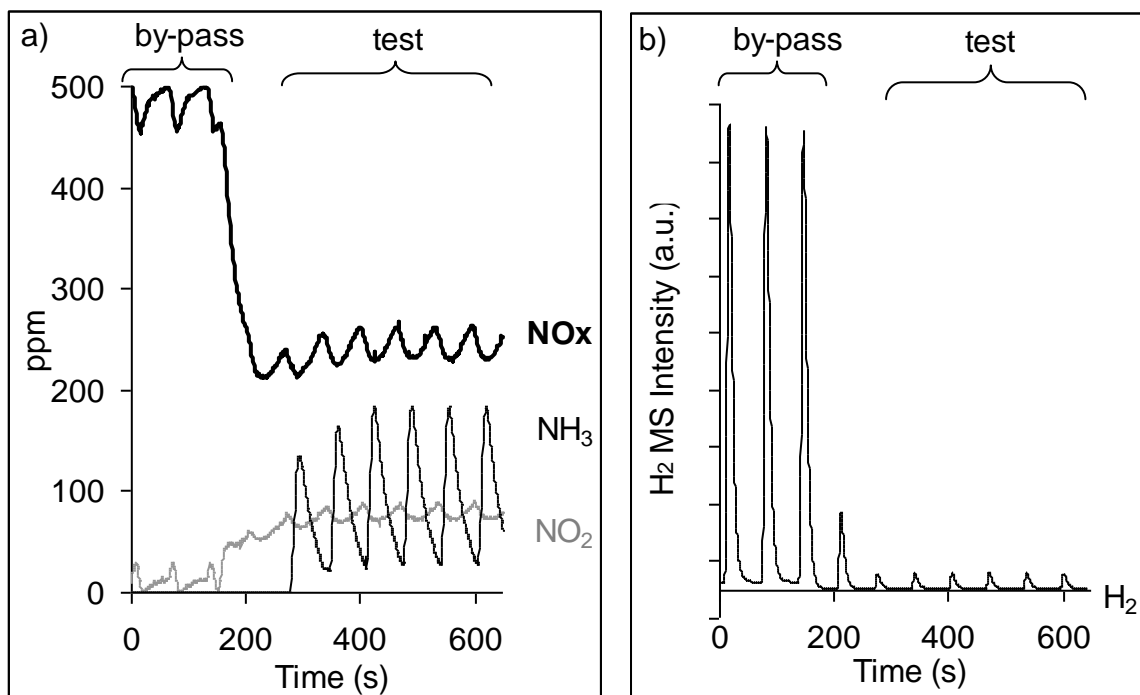


Figure 2: Typical storage-reduction experimental curves. Results obtained on Pt/10Ba/Al at 400°C with 3%H₂ in the rich pulse. a) NO_x, NO₂ (chemiluminescence) and NH₃ concentrations (FTIR multigas analyzer), b) H₂ signal (mass spectrometer).

Table 3: NO_x removal efficiency tests: NO_x conversion, selectivity in N-compound and H₂ consumption.

catalyst	Pt/10Ba/Al			Pt/10BaFe/Al			Pt/10BaMn/Al				
temperature test (°C)	200	300	400	200	300	400	200	300	400	400	400
H ₂ in the rich pulse (%)	3	3	3	3	3	3	3	3	3	6	9
NO _x conversion (%)	20	39	46	17	21	33	20	34	41	97	97
N ₂ selectivity (%)	80	78	81	79	76	80	83	77	97	99	93
NH ₃ selectivity (%)	20	22	19	21	24	20	17	23	3	1	7
H ₂ consumption (%)	88	95	98	86	92	99	84	97	100	100	87

Conclusion

Compared to Pt/10Ba/Al, Fe addition leads to a small increase in NO_x storage capacity, and more interestingly to a better sulfur regeneration due to bulk barium sulfate formation inhibition. Unfortunately, the NO_x storage property is not fully recovered after the sulfur regeneration. Moreover, Fe addition induces rather a degradation of the NO_x removal efficiency under rich/lean cycling conditions, especially at high temperature. Mn addition also improves the NO_x storage capacity, but no significant influence on the sulfur elimination

is observed. With 3% H₂ in the rich pulse, slightly lower NO_x conversion is obtained at 400°C with the Mn-doped catalyst, but, compared to Pt/10Ba/Al, the NH₃ selectivity is drastically decreased from 20% to 3%. The NO_x conversion can be improved over the Mn-based catalyst, always keeping a low NH₃ selectivity, by increasing H₂ concentration in the rich pulse. 6% H₂ is determined as the optimal concentration under our test conditions between the ammonia formation rate and the amount of stored NO_x.

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