



# Ptbamnce/Al as a High-Efficiency Catalyst for Nox Storage and Reduction as a Function of Cycling Conditions



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## Abstract

The aim of the study was to present novel PtBaMnCe/Al material as the high-efficiency catalyst for NO<sub>x</sub> storage and reduction (NSR) application. In the first part of this paper, the performance of PtBaMnCe/Al catalyst on the NO<sub>x</sub> conversion to N<sub>2</sub> was presented. Compared with traditional model PtBa/Al catalyst, the PtBaMnCe/Al catalyst exhibit at least 2 times higher in NO<sub>x</sub> conversion efficiency at 400 oC. More interesting, ammonia yield on PtBaMnCe/Al is limited to a very lower level (nil). With 6% H<sub>2</sub> in the rich pulse, the 94% of NO<sub>x</sub> conversion to N<sub>2</sub> can be obtained with PtBaMnCe/Al catalyst at 400 oC. The second part deals with sulfur resistance of PtBaMnCe/Al catalyst. Sulfur poisoning, regeneration of sulfated catalysts and NO<sub>x</sub> removal efficiency under rich/lean cycling conditions are studied. PtBaMnCe/Al is more sulfur resistant than PtBa/Al. However, the sulfur poisoning is irreversible and only 85% of the initial NO<sub>x</sub> conversion could be recovered after the regeneration treatment.

**Keywords:** Emission Control; Lean Burn; NO<sub>x</sub> Storage and Reduction; Sulfur in Fuel; Lean/rich cycle

## Introduction

Lower CO<sub>2</sub> 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<sub>x</sub> in excess of O<sub>2</sub>, which makes NO<sub>x</sub> reduction into N<sub>2</sub> very difficult. One possible solution is the use of the NO<sub>x</sub> storage reduction (NSR) catalyst [ -3], working in transient periods: during the lean condition, NO<sub>x</sub> are firstly oxidized and stored as nitrites or nitrates on a basic material, usually barium oxide. Periodically, the catalyst is regenerated: the stored NO<sub>x</sub> (NO<sub>2</sub>) are reduced in N<sub>2</sub> 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 [2,3], and ammonia emission can be formed during the short excursion under rich conditions, especially when hydrogen is used as reducer [ -6].

In our previous study [5], ammonia intermediate pathway was clearly demonstrated for the reduction of the stored NO<sub>x</sub> with H<sub>2</sub>. It appears that, when hydrogen is missing in the rich pulses, that are fully converted, the ammonia selectivity tends to be nil because the produced NH<sub>3</sub> can react with the remaining stored NO<sub>x</sub>. In opposition, if some hydrogen remains, the ammonia selectivity increases with the amount of excessive hydrogen. It induces that NO<sub>x</sub> reduction with H<sub>2</sub> into ammonia is faster than

the NO<sub>x</sub> selective catalytic reduction with ammonia. This is a fundamental result for our next step: catalyst modification for a better NO<sub>x</sub> conversion to N<sub>2</sub>.

In the first part of this paper, our latest result in catalyst improvement with a multi-component PtBaMnCe/Al sample will be presented. In the second part of this paper, the impact of sulfur in gasoline on the performance of NSR catalyst will be discussed. Sulfur poisoning, regeneration of sulfated catalysts and NO<sub>x</sub> removal efficiency under rich/lean cycling conditions are studied [7].

## Experimental

### Catalyst preparation

The detailed preparation protocols are reported in our previous studies [8]. The reference catalyst contains 1 wt% Pt and 20 wt% BaO supported on alumina. Alumina powder (230 m<sup>2</sup>.g<sup>-1</sup>) was immersed in an ammonia solution and was firstly impregnated using a barium nitrate salt. After evaporation at 80 oC and drying at 120 oC, the obtained powder was treated at 700°C under synthetic dry air. Platinum was then impregnated using a Pt (NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> aqueous solution. After drying, the catalyst was pre-treated at 700 oC for 4h under N<sub>2</sub>, and finally

stabilized at 700 oC for 4h under a mixture containing 10% O<sub>2</sub>, 5% H<sub>2</sub>O in N<sub>2</sub>. The modified samples were prepared using the same protocol except that the nitrate salts of Mn(IV), and Ce (III) were simultaneously added with the barium salt. In this case, a part of alumina was replaced to assure the desired “additive/Ba” molar ratio. The catalysts containing both Mn and Ce were also prepared. In this case, Mn/Ba and Ce/Ba molar ratio are always 1. The Mn–Ce modified catalysts are noted PtBaMnCe/Al.

**Catalytic activity measurements: NOx conversion in cycling conditions**

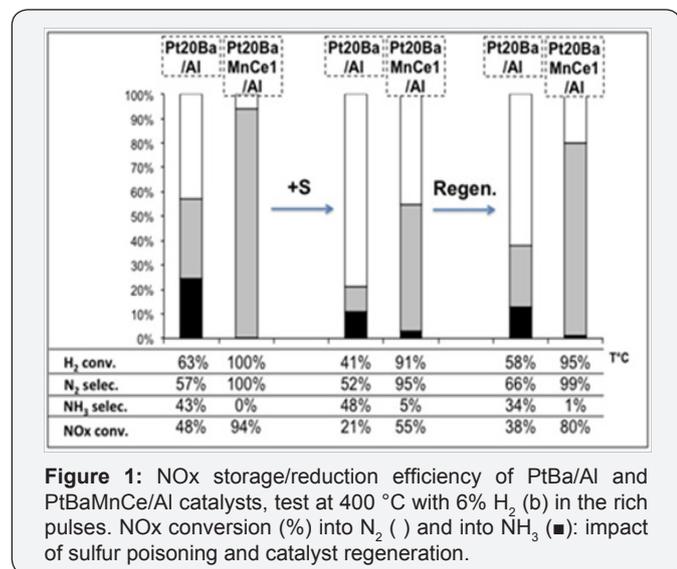
**Table 1:** Rich and lean gas compositions used for the NOx conversion test (60s lean/3s rich). Total flow rate: 10 L. h<sup>-1</sup>.

Gas	NO	H <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	N <sub>2</sub>
Rich	-	3-6%	-	10%	10%	Balance
Lean	500 ppm	-	10%	10%	10%	Balance

Before measurement, the catalyst (60mg) was pre-treated in situ at 450 oC under 3% H<sub>2</sub>, 10% H<sub>2</sub>O, 10% CO<sub>2</sub> and N<sub>2</sub> for 15min. The sample was then cooled down to 400 oC under the same mixture. The NOx conversion was studied in cycling condition by alternatively switching between lean (60s) and rich (3s) conditions using electro-valves. The gas composition is described

**Table 2:** NOx storage/reduction efficiency test at 400 oC with 3% H<sub>2</sub> (a) or 6% H<sub>2</sub> (b) in the rich pulses.

Catalyst	3%H <sub>2</sub> in the rich pulse				6%H <sub>2</sub> in the rich pulse			
	H <sub>2</sub> conversion (%)	NOx conversion (%)	N <sub>2</sub> selectivity (%)	NH <sub>3</sub> selectivity (%)	H <sub>2</sub> conversion	NOx conversion (%)	N <sub>2</sub> selectivity (%)	NH <sub>3</sub> selectivity (%)
PtBa/Al	85	45	67	33	63	48	57	43
PtBaMnCe/Al	100	70	100	0	99	94	100	0



**Figure 1:** NOx storage/reduction efficiency of PtBa/Al and PtBaMnCe/Al catalysts, test at 400 °C with 6% H<sub>2</sub> (b) in the rich pulses. NOx conversion (%) into N<sub>2</sub> (□) and into NH<sub>3</sub> (■): impact of sulfur poisoning and catalyst regeneration.

Thus, with this condition with full H<sub>2</sub> conversion, the in situ formed ammonia is able to react with the remaining stored NOx to produce N<sub>2</sub>. With 6% H<sub>2</sub> in the rich pulses (Table 1), a significant NOx conversion improvement is observed with PtBaMnCe/Al sample, from 70% to 94%. These values can be considered as optimal values since the NOx storage rates of this sample

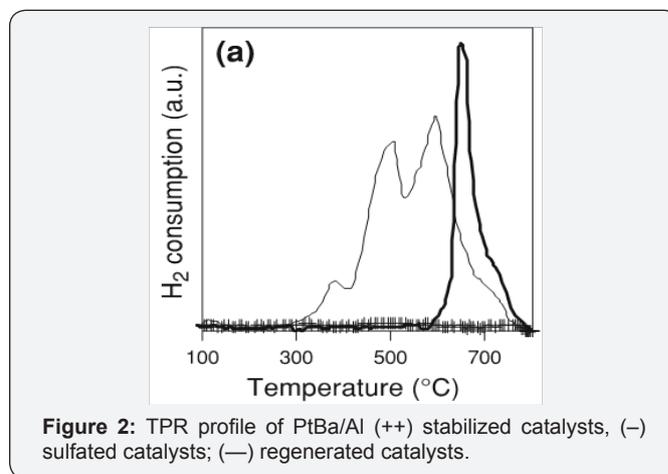
(Table 1). NO and NO<sub>2</sub> were followed by chemiluminescence, N<sub>2</sub>O by specific FTIR, H<sub>2</sub> by mass spectrometry. Before the analyzers, H<sub>2</sub>O was trapped in a condenser at 0 oC. The trapped water was analyzed by two different HPLCs for NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>. NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> were added to the unconverted NOx. The N<sub>2</sub> selectivity is calculated assuming no other N-compounds than NO, NO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>.

**Results and Discussions**

**NOx storage-reduction efficiency of PtBaMnCeX/Al catalyst**

The influence of cerium-manganese addition on the NOx storage-reduction efficiency of PtBa/Al was studied at 400 oC using first 3% H<sub>2</sub> in the rich pulses. For comparison, results obtained with the PtBa/Al reference catalyst are also reported in (Figures 1 & 2). At 400 oC with 3% H<sub>2</sub> in the rich pulses, the hydrogen conversion reaches 100% with PtBaMnCe/Al catalyst (Table 2). Hence, the NOx conversion could be limited by the reducer amount. However, the NOx conversion to NH<sub>3</sub> over this sample is higher than PtBa/Al catalyst. More interestingly, the ammonia selectivity becomes nil with PtBaMnCe/Al catalyst.

reach 96% (result not shown). For the reference catalyst, the increase of H<sub>2</sub> content in the rich pulse only leads to an increase in NH<sub>3</sub> selectivity. This study shows that PtBaMnCe/Al catalyst is very promising for NOx storage-reduction application. Most importantly, the NH<sub>3</sub> yield is very low (nil) with this catalyst. Mn-Ce addition in NSR catalyst leads to the enhancement of the catalytic properties. It can be attributed to an improvement of the reaction between the ammonia formed in situ and the remaining stored NOx [6].



**Figure 2:** TPR profile of PtBa/Al (++) stabilized catalysts, (–) sulfated catalysts; (—) regenerated catalysts.

## Impact of sulfur in gasoline on the performance of model NSR catalyst

In this section, the impact of sulfur on the performance of model NSR catalyst is focused. Firstly, the NSR catalyst was sulfated before catalytic activity measurement in order to simulate the deposition of sulfur compound in gasoline onto the catalyst surface. And then, the regeneration of sulfated catalyst was studied. The sulfating treatment was performed at 300 oC with SO<sub>2</sub> 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 oC for 30min under rich conditions with a mixture containing 2.5% H<sub>2</sub>, 10% CO<sub>2</sub>, and 10% H<sub>2</sub>O in N<sub>2</sub>.

### SO<sub>2</sub> poisoning and regeneration

The NO<sub>x</sub> conversion rate of the fresh, sulfated and after sulfur regeneration treatment of Pt20Ba/Al and Pt20BaMnCe1/Al catalysts, measured at 400°C, are reported in Figure 1. After the sulfating treatment, the NO<sub>x</sub> storage-reduction capacities strongly decrease. For Pt20Ba/Al, a loss of 56% is observed. Mn-Ce doped sample is more resistant toward the poisoning treatment, with a loss of 41%. After the regeneration treatment, only 79% of the initial value is recovered over Pt20Ba/Al, indicating that an efficient regeneration of the NO<sub>x</sub> storage sites cannot obtain. This rate is slightly higher for Pt20BaMnCe/Al (85%) [9,10].

The sulfated Pt20Ba/Al catalyst was characterized by H<sub>2</sub>-TPR (Figure 2). The sample was first in situ pretreated at 300 oC under pure oxygen. The reduction was carried out with 1% H<sub>2</sub> from room temperature up to 800 oC. As described in [4], the TPR profile of the sulfated Pt/10Ba/Al catalyst exhibits two main peaks around 500 and 600 oC. 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 oC, is ascribed to the reduction of surface barium sulfates, and the observed shoulder near 750 oC corresponds to bulk barium sulfate reduction.

Assuming a H<sub>2</sub>/SO<sub>4</sub><sup>2-</sup> ratio of 4 for the sulfate reduction (X-SO<sub>4</sub>+4H<sub>2</sub>-->X-S+4H<sub>2</sub>O and/or X-SO<sub>4</sub>+4H<sub>2</sub>--->X-O+H<sub>2</sub>S+3H<sub>2</sub>O), total sulfur content can be deduced from hydrogen consumption. After the sulfur regeneration, only 58% of the deposited sulfur is removed. Moreover, a stabilization of the remaining sulfates is observed. This result indicates that the sulfur poisoning is irreversible. 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 PtBaMnCe/Al catalyst was also observed after the sulfur regeneration treatment without previous sulfating procedure.

## Conclusion

In the first part of this study, it was shown that Ce, Mn addition to PtBa/Al led to an improvement of the NO<sub>x</sub> reduction (conversion and selectivity). A near total NO<sub>x</sub> conversion to N<sub>2</sub> can be observed at 400 oC with PtBaMnCe/Al. In the second part, the effect of sulfur in the gasoline on the catalyst performance was observed. The sulfur resistance of PtBaMnCe/Al catalyst is higher than reference PtBa/Al catalyst. Unfortunately, the NO<sub>x</sub> storage-reduction property cannot be fully recovered after the sulfur regeneration. These results clearly indicate that the lower sulfur level in fuels is indispensable for current and future emission control systems.

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