

# Innovative Hybrid Rare Earth and Barium Materials with Enhanced Properties for NO<sub>x</sub> Storage Applications

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## ABSTRACT

The reduction of NO<sub>x</sub> to meet current diesel regulation standards has been achieved using two main technologies named NH<sub>3</sub>-SCR and LNT. In the forthcoming years, the implementation of new and colder test cycles such as “real driving emissions” (RDE), combined with CO<sub>2</sub> targets (95 g/km is 2020 target in Europe) will require higher NO<sub>x</sub> storage capacity (NSC) in the low temperature region (120-350°C). On the other hand, lean-burn Gasoline vehicles, emitting exhaust gases at higher temperatures, will require improved NSC over a broader temperature range (200-500°C). Therefore, the development of more efficient NSC materials is an area of extensive study by original equipment manufacturers (OEMs), catalysts manufacturers, and raw materials suppliers. Today, ceria is a key component in the formulation of active NSC washcoats. It is often combined with barium in order to improve its high temperature NSC, but this also leads to a significant loss of specific surface area and thus a decrease in overall performance at low temperature. This paper reports recent progress made on NSC materials, with the aim to enlarge their operational temperature window. In this regard, Solvay has developed an innovative solution: rare earth and barium hybrid compounds as advanced NSC materials. synthetic gas bench tests performed on powder model catalysts show a significant increase in NSC at low temperatures and a very strong benefit in NSC at high temperatures, compared to current Solvay reference ‘High Stability Ceria’ or Ba-doped ceria.

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## INTRODUCTION

The removal of nitrogen oxides (NO<sub>x</sub>) from diesel exhaust gas to comply with the current emission standards (EURO6, LEVIII) is a very challenging task. So far, two main technologies have been implemented for the reduction of the NO<sub>x</sub> under fuel-lean conditions:

- i. Selective catalytic reduction (SCR) of NO<sub>x</sub> using NH<sub>3</sub> as the reductant. This technology was initially developed for the NO<sub>x</sub> abatement of stationary sources [1] using vanadium-based catalysts. It has been successfully applied in the last decade on trucks in Europe and examined in the US [2]. The NH<sub>3</sub>-SCR process has generated great interest for passenger car applications as well [3, 4]. To comply with the latest regulation standards, the diesel fleet displaying engines over 1.6-2 L in Europe and in the US will be equipped with a SCR brick, mainly using Fe- or Cu- exchanged zeolites. The main drawbacks of this technology are an additional tank for the Adblue solution (NH<sub>3</sub> precursor) and the lower thermal limit of 180°C for effective injection and utilisation, preventing NO<sub>x</sub> abatement at low temperature.
- ii. Lean NO<sub>x</sub> trap (LNT) or NO<sub>x</sub> storage / reduction (NSR) catalyst [5, 6, 7]. This technology was initially developed by Toyota in the early 90s, and operates upon the principle of lean/rich cycles. Under lean conditions (several minutes) NO<sub>x</sub> are stored in the form of NO<sub>3</sub><sup>-</sup>, and subsequently released and reduced to N<sub>2</sub> during short rich events (several seconds) obtained by

modification of engine parameters to produce higher engine out CO and HC<sub>s</sub>. The first generation of LNT catalysts comprised PGM, barium and alumina [8]. Subsequently, the incorporation of ceria into the formulation was investigated and was demonstrated to provide significant benefits. Indeed, ceria improves the sulfur tolerance of the LNT catalyst by trapping some of the sulfur species thus limiting their accumulation on BaO [9,10]. This property allows the extension of the operating period between regeneration events, leading to lower fuel penalty and lower PGM sintering. The resistance against Pt sintering is also believed to be improved in the presence of ceria owing to the formation of Pt-O-Ce bonds [11, 12, 13], well-known in the three way catalyst (TWC) technology used for gasoline vehicles. Moreover, ceria has been shown to improve the efficiency for NO<sub>x</sub> storage and reduction, particularly in the low temperatures region [14,15]. Additionally Pt-Ceria is able to catalyze water gas shift (WGS) under rich conditions thereby producing H<sub>2</sub> [16,17] which is beneficial for both sulfur regeneration and NO<sub>x</sub> reduction since H<sub>2</sub> has been shown to be a better reductant than CO for both reactions [18, 19, 20]. Nowadays, conventional LNT catalyst is composed of Pt/alumina-ceria-barium oxide and Rh/alumina. The main drawbacks of this technology are PGM cost, fuel penalty owing to rich events, and strong sulfur poisoning. LNT is preferred for engines smaller than 1.6-2 L and is more extended in Japan.

In the forthcoming years, different factors will require the development of even more efficient NO<sub>x</sub> abatement materials and strategies for lean-burn vehicles. Each standard evolution leads to more and more stringent emission limits. Next, the implementation of new test procedures e.g. “real driving emissions” (RDE) or the “worldwide harmonized light duty driving test cycle” (WLTC), will result in an extended engine and hence catalysts operation area. NO<sub>x</sub> aftertreatment will become more challenging, mostly at low temperature. In addition implementation of the European CO<sub>2</sub> emission target of 95 g/km by 2020 will further challenge system performance. Therefore, exhaust aftertreatment system will require higher NO<sub>x</sub> storage capacity (NSC) in the low temperature region (120–350°C). In the recent MinNO<sub>x</sub> Conference (Berlin, June 2014), the development trends of future exhaust architectures presented by OEMs and catalysts manufacturers [21, 22, 23, 24, 25] showed a growing need to add a NO<sub>x</sub> scavenger function in the diesel oxidation catalyst (DOC) brick, generally combined with a SCR (or SCR-on-DPF) catalyst located downstream (Figure 1). Optimizing the NO<sub>x</sub> abatement activity by combination of NSC and SCR is a highly challenging task with regards to the NSC catalyst design, requiring a fine tuning of its surface properties. As discussed, the NSC has to both store NO<sub>x</sub> in the low temperature region but also facilitate NO<sub>x</sub> release in a temperature window appropriate to the SCR design to enable the efficient conversion of NO<sub>x</sub> in the SCR brick.

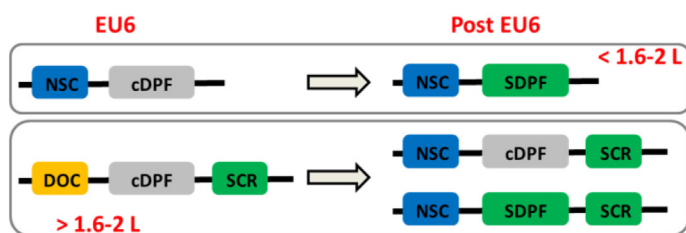


Figure 1. Simplified expected development trends for diesel exhaust gas aftertreatment in Europe.

On the other hand, lean-burn gasoline vehicles, emitting exhaust gases at higher temperatures, will need improved NSC over a broad temperature region (200–500°C).

For these diverse reasons NO<sub>x</sub> emission control will remain amongst the most challenging to manage. To tackle this issue, a strong renewal of interest of improved NSC materials has developed in the last couple of years.

Today, ceria is a key component in NSC technologies, and is often combined with barium oxide in the catalyst formulation, with the aim to improve its basicity and thus NSC at high temperatures. In this regard, herein we report the recent progress in the field of Ba-doped ceria materials. Innovative formulations and synthesis processes were developed to both increase aged surface area and to finely tune the acido-basic properties of these materials. Via these objectives it becomes possible to enhance both low and high temperature NSC, whilst maintaining appropriate NO<sub>x</sub> release and desulfation capacity.

## 2. EXPERIMENTAL

### 2.1. Materials

**Basic ceria samples.** The catalytic activities of two new samples, ‘Improved Basic Ceria 1’ and ‘Improved Basic Ceria 2’, are discussed in the paper. Both contain Ba but consist of different compositions. The materials are prepared by proprietary methods. Improved basic ceria 1 and improved basic ceria 2 are designed to target NO<sub>x</sub> storage applications for passenger cars or light duty vehicles, for either diesel or lean-burn gasoline exhaust aftertreatment systems.

The materials developed and commercialized by Solvay are oxides in powder form. In this paper, the oxides were also impregnated with 1% Pt by mass using incipient wetness impregnation. Prior to impregnation, the oxides were all calcined in air at 800°C for 4h.

### 2.2. Material Characterization

**Specific surface area** was measured using the BET method after pretreatment at 200°C for 2 h. Unless otherwise specified, the oxide surface area is measured after 4 h dry air calcination of 5 g oxide in a muffle furnace at 800°C. The BET surface area for the Pt-loaded catalysts was determined after hydrothermal treatment at 700°C in air + 10% water for 4 h.

**X-Ray Diffraction** was performed on a Goniometer Panalytical X’Pert Pro MPD, using a copper source, variable slits, an X celerator detector, and a nickel filter at the back. Measurements were made for 2θ = 5° to 90° at 200 seconds per 0.017° step.

**Sulfur dosing** was performed on a Horiba EMIA 320-V2, using iron and LECOCEL as combustion accelerators. The sulfur pick-up is expressed in weight percentage based on the catalyst total weight.

**Lean aging treatment** was performed for the Pt-loaded powder catalysts (2 g) applying hydrothermal conditions of 10 vol.% O<sub>2</sub>, 10 vol.% H<sub>2</sub>O and balance N<sub>2</sub> (total flow = 24 L/h) at 700°C for 4 h. These parameters were selected to simulate severe lean conditions.

**Lean sulfation aging treatment** was optionally performed for the Pt-loaded powder model catalysts (0.4 g), subsequently to lean aging treatment, applying hydrothermal conditions of 10 vol.% O<sub>2</sub>, 10 vol.% H<sub>2</sub>O, 20 ppm SO<sub>2</sub> and balance N<sub>2</sub> (total flow = 15 L/h) at 300°C for 12 h. These parameters were selected to simulate severe lean sulfation conditions.

## 3. METHODS

The NO<sub>x</sub> storage capacity and release behaviors of the catalysts were investigated under different conditions by ‘simplified’ testing of model powder catalysts.

**Testing of the model powder catalyst** was performed on a synthetic gas bench with a space velocity of 25 000 h<sup>-1</sup> according to two different test methodologies described below. In all cases, the aged catalyst (150 mg) was introduced in a quartz U-shaped down-flow reactor (length: 225 mm, internal diameter: 4 mm). The composition of the outlet gases was monitored on line by a Fourier Transform InfraRed (FTIR) spectrometer.

**Low temperature NSC test** was performed on lean aged catalysts and comprised two steps. First, lean NO<sub>x</sub> storage was determined by uptake at 120°C for 90 min under the gas composition detailed in Table 1. Second, lean NO<sub>x</sub> release was monitored under the same gas composition with the exception of NO<sub>x</sub> by raising the temperature up to 600°C. All gases were controlled using mass flow controllers.

Table 1. Gas composition in vol% of the low temperature NO<sub>x</sub> storage and NO<sub>x</sub> release testing.

| Gas composition vol.% | Lean NO <sub>x</sub> storage | Lean NO <sub>x</sub> release |
|-----------------------|------------------------------|------------------------------|
| NO                    | 0.014                        | -                            |
| NO <sub>2</sub>       | 0.018                        | -                            |
| H <sub>2</sub> O      | 5                            | 5                            |
| CO <sub>2</sub>       | 5                            | 5                            |
| O <sub>2</sub>        | 10                           | 10                           |
| N <sub>2</sub>        | Balance                      | Balance                      |

**NSC in range 200-400°C test** was performed on lean sulfation aged catalysts, and was composed of two steps. First, the catalyst was activated under rich conditions at 600°C for 20 min under the gas composition detailed in Table 2. Second, NO<sub>x</sub> storage capacity was investigated under lean conditions at different temperatures ranging from 200 to 400°C. The different gas compositions, detailed in Table 2, were again controlled by mass flow controllers.

Table 2. Vol% Gas composition for NO<sub>x</sub> storage tests 200-400°C.

| Gas composition vol.%         | Rich activation | Lean NO <sub>x</sub> storage |
|-------------------------------|-----------------|------------------------------|
| C <sub>3</sub> H <sub>6</sub> | 0.025           | -                            |
| C <sub>3</sub> H <sub>8</sub> | 0.025           | -                            |
| CO <sub>2</sub>               | 3               | 5                            |
| H <sub>2</sub> O              | 5               | 5                            |
| O <sub>2</sub>                | 5               | 10                           |
| CO                            | 10              | -                            |
| NO                            | -               | 0.030                        |
| NO <sub>2</sub>               | -               | -                            |
| N <sub>2</sub>                | Balance         | Balance                      |

**Lean Desulfation capacity** was measured by DTA-TGA on a Mettler LIF 1600 Thermobalance coupled to a Mass Spectrometer. The samples were analyzed under air, from 100 up to 1200°C with a temperature ramp of 10°C/min.

**Rich Desulfation capacity** was evaluated by comparing the amount of sulfur species (sulfur dosing) on the catalyst after lean sulfation aging, and after the activation step (rich conditions, 20 minutes at 600°C) of the NSC test at 200°C.

## 4. RESULTS AND DISCUSSION

### 4.1. High Stability Ceria: NSC Key Component

Today, Solvay high stability ceria is a key component in the formulation of LNT / NSC catalysts for low temperature NO<sub>x</sub> storage applications. The benefits of this material to conventional Ba-doped alumina based catalysts are summarized in this section.

Figure 2 shows the NO, NO<sub>2</sub> and total NO<sub>x</sub> storage efficiency at low temperature (120°C) obtained for high stability ceria and Ba-doped alumina (20 wt% BaO and 80 wt% Al<sub>2</sub>O<sub>3</sub>) catalysts after hydrothermal aging. Similar NSC was observed, but high stability ceria allows for significantly higher NO abatement. This is significant for operation in low load or in low temperature regimes e.g. during cold start or urban driving, since the engine out NO<sub>x</sub> mainly comprises NO. Therefore, this peculiar property of high stability ceria is of special interest for low temperature NO<sub>x</sub> storage applications.

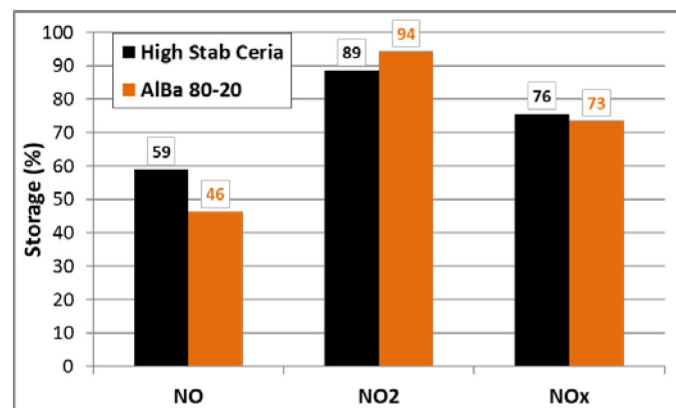


Figure 2. NO, NO<sub>2</sub> and NO<sub>x</sub> storage at 120°C after 2 minutes - Pt-loaded catalysts after hydrothermal aging.

Figure 3 illustrates the NO<sub>2</sub> release profiles vs temperature, under lean conditions, subsequent to a 90 minutes period of NO<sub>x</sub> storage at 120°C. The results obtained revealed a clearly different behavior for these two catalysts. Thus Ba-doped alumina exhibits a single-peak profile centered at 460°C, with full NO<sub>2</sub> desorption at 560°C, reflecting the role of the strongly basic sites of the barium. This constitutes a severe drawback for this formulation as the regeneration of these highly stable adsorption sites requires temperatures much higher than the average diesel exhaust gas temperature. In contrast, the high stability ceria based catalyst displays a double-peak profile, shifted to significantly lower temperatures. The first peak, centered at 220°C, is attributed to ceria in intimate interaction with platinum. The second one, centered at 335°C, is attributed to ceria spatially discrete from the influence of platinum. This material starts releasing NO<sub>2</sub> around 120°C (versus 280°C) and allows for full desorption at 430°C (versus 560°C).

Table 3 summarises the sulfur pick-up of the catalysts after a sulfation aging at 300°C for 12h (expressed in weight percent), and the desulfation rate achieved at 600°C under rich conditions. The results show that the Ba-doped alumina based catalyst adsorbs higher amounts of sulfur (+40%). Moreover, owing to the strong basic sites