



## Review

Carbon–NSR catalyst interaction: Impact on catalyst structure and NO<sub>x</sub> storage efficiencyJennifer Klein<sup>a</sup>, Dongliang Wu<sup>a</sup>, Valerie Tschamber<sup>a,\*</sup>, Ioana Fechete<sup>b</sup>, Francois Garin<sup>b</sup><sup>a</sup> Laboratoire Gestion des Risques et Environnement, Université de Haute Alsace, 3b rue A. Werner, 68093 Mulhouse Cedex, France<sup>b</sup> Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse, Université de Strasbourg, UMR 7515 CNRS, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France

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## ABSTRACT

The impact of the presence of carbon on the structure of model NO<sub>x</sub> storage catalysts (NSR) and their ability to store NO<sub>x</sub> were investigated. Three catalysts, composed of Pt and/or Ba supported on Al<sub>2</sub>O<sub>3</sub>, were prepared. Reactivity of the catalysts toward NO<sub>x</sub> storage was studied during adsorption/TPD cycles. Comparison of the results obtained in the presence and absence of carbon in the catalytic bed revealed that a carbon–catalyst contact leads to a decrease in NO<sub>x</sub> storage capacity attributed to a destabilization of nitrate species formed far from Pt sites. Both Al and Ba sites are affected. During the carbon oxidation process, an aging of the catalysts, caused by Pt sintering and Ba agglomeration, as observed using TEM technology. These structural modifications reduce the proximity between the Pt sites and adsorption sites (Ba and/or Al), which results in a decrease in the NO<sub>x</sub> storage toward the 'nitrite route'.

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## 1. Introduction

The use of after-treatment devices to reduce NO<sub>x</sub> and soot emissions generated by diesel engines is currently mandatory to meet European standards. To control soot emissions, diesel particulate filters (DPF) are typically used. This technology traps soot, which must then be removed to maintain filtration capacity. Regeneration

of the filter, which is the crucial step of this technology, is usually based on the oxidation of deposited soot either by O<sub>2</sub> and/or by the gas mixture NO<sub>2</sub>/O<sub>2</sub>. When using O<sub>2</sub> as oxidant, the presence of a ceria-based catalyst, associated with the soot particles and/or deposited on the filter walls, is necessary to achieve a sufficient gasification rate. To improve this rate even further, a periodical extra-fuel injection is usually performed so that the exhaust gas temperature increases. However, this process leads to excess fuel consumption. As NO<sub>2</sub> is a better oxidant than O<sub>2</sub>, its presence in the gas flow allows soot oxidation at a lower temperature (above 250 °C) [1–3]. Thus, with a gas stream composed of a mixture of NO<sub>2</sub>

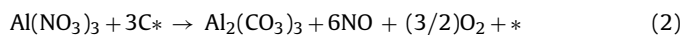
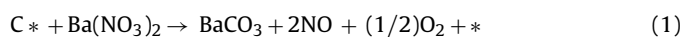
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and O<sub>2</sub>, continuous soot combustion in the filter can be obtained in the average temperature range of diesel exhaust (300–400 °C) [4–6]. However, because NO<sub>2</sub> is present in the diesel exhaust stream at a low concentration (5–15% of total NO<sub>x</sub>), a diesel oxidation catalyst (DOC), placed upstream of the particulate filter or as a coating on the channel walls of the diesel particulate filter, is necessary to oxidize NO to NO<sub>2</sub>. The DOC generally implemented is a Pt-based catalyst. Such a process was used in the continuous regeneration trap (CRT) technology proposed by Johnson Matthey [7]. The mechanism involved in the oxidation of soot by a NO<sub>2</sub>/O<sub>2</sub> mixture is now well established and consists of two main reactions occurring simultaneously: a direct reaction between carbon and NO<sub>2</sub> and a cooperative reaction simultaneously involving O<sub>2</sub> and NO<sub>2</sub> [3,6]. In the latter case, NO<sub>2</sub> adsorbs on –C(O) complexes resulting from O<sub>2</sub> chemisorption to form nitro-oxygenated intermediate species, which are then decomposed by NO<sub>2</sub> [6,8]. Both the direct and the cooperative reactions lead to carbonaceous material combustion with CO<sub>2</sub> and CO formation and NO<sub>2</sub> reduction to NO. Several studies performed at a laboratory scale revealed that when soot is in contact with the DOC, an enhancement of the cooperative reaction rate occurs. Jeguirim et al. [9,10] proposed that besides the well-known catalytic reoxidation of NO into NO<sub>2</sub>, Pt also exerts a catalytic effect on the cooperative carbon–NO<sub>2</sub>–O<sub>2</sub> oxidation reaction. It acts on the cooperative reaction by enhancing the formation of atomic oxygen, which is then transferred to the carbon surface.

Two different technologies were developed to reduce NO<sub>x</sub> emission in an oxygen-rich environment: selective catalytic reduction (SCR) and NO<sub>x</sub> storage reduction (NSR). The latter technology is more suited for passenger cars and works under cyclic conditions alternating lean periods during which NO<sub>x</sub> is stored as nitrate on the catalyst and shorter rich periods during which nitrates are desorbed and reduced to N<sub>2</sub>. The behavior of NSR catalysts or model NSR catalysts, such as Pt–Ba/Al<sub>2</sub>O<sub>3</sub>, Pt–K/Al<sub>2</sub>O<sub>3</sub> or Pt–K–Ba/Al<sub>2</sub>O<sub>3</sub>, is well documented in the literature. In the last decade, several papers have focused on the NO<sub>x</sub> storage mechanism [11–14]. It is generally admitted that the first stage consists of the oxidation of NO into NO<sub>2</sub> on platinum (Pt) sites. Olsson et al. [11] proposed that NO<sub>2</sub>(g) is then loosely bound to BaO sites, leading to the formation of BaO–NO<sub>2</sub> intermediaries that decompose on BaO<sub>2</sub> to release NO(g). This step is then followed by nitrate formation resulting from the adsorption of NO<sub>2</sub> gas on BaO<sub>2</sub> sites. Previously, Mazhoul et al. [13] concluded that Pt sites close to barium sites allow nitrate formation, while Pt sites far from barium sites are responsible for NO oxidation. Nova et al. [12] recently proposed, in accordance with these results, a more detailed mechanism with two distinct routes: a ‘nitrite route’ and a ‘nitrate route’. The ‘nitrite route’ implies the oxidation of NO on Pt sites followed by the formation of nitrite ad-species on Ba neighboring Pt sites. Nitrite ad-species are then progressively oxidized into nitrate species, which prevail at saturation. Accordingly, a cooperative interaction between Pt and a nearby Ba site is important for this route and Pt plays a role in both the formation of nitrites and their subsequent oxidation to nitrates. Conversely, the ‘nitrate route’ corresponds to NO<sub>2</sub> storage on BaO, directly in the form of nitrates without proximity between the Ba and Pt sites. This route implies the release of one NO molecule for three molecules of NO<sub>2</sub> consumed. Nova et al. [12] proposed that both the ‘nitrite’ and ‘nitrate’ routes occur simultaneously during NO/O<sub>2</sub> storage.

To decrease the size of the after-treatment devices assembled along the exhaust line and the induced backpressure, Toyota [15] developed the diesel particulate NO<sub>x</sub> reduction (DPNR) system. This system is composed of a particulate wall-flow filter coated with an NSR catalyst layer and works under cyclic conditions. Particulate filter regeneration is supposed to be effective during the lean phase due to the presence of NO<sub>x</sub> and the excess of oxygen in the exhaust gas, similarly to CRT technology. It is also claimed

that soot oxidation occurs during the rich phase [15]. Then, soot treatment, NO<sub>x</sub> reduction and CO and hydrocarbon oxidation functions are coupled on a single monolith, leading to this technology being named a ‘4-way catalytic converter’. Combination of NSR and CRT technologies modifies their behavior, so recent studies have investigated the reaction mechanism of 4-way catalytic materials [16–23]. Most of these investigations were focused on the influence of the presence of a model NSR catalyst (Pt–Ba/Al<sub>2</sub>O<sub>3</sub> or Pt–K/Al<sub>2</sub>O<sub>3</sub>) on soot oxidation and concluded that NO<sub>x</sub> storage function enhanced soot combustion either by decreasing the soot oxidation temperature and/or by increasing the local NO<sub>2</sub> gas phase concentration [17,20–22]. While several authors [18–23] observed that the NO<sub>x</sub> storage capacity of the NSR catalyst was partially inhibited by the presence of soot, only a few of them [18,19,22,23] investigated the soot–NSR catalyst interaction and its influence on the NO<sub>x</sub> storage mechanism. In our previous work, participation of the following direct surface reaction between carbon particles and NO<sub>x</sub> storage sites to form adsorbed carbonate species was proposed:



Our results showed that carbon contact with the NO<sub>x</sub> storage catalyst affects nitrate species formed by the ‘nitrate route’ (far from Pt sites) more than those formed by the ‘nitrite route’.

The purpose of this study was to investigate more precisely the effect of the interaction between carbon and model NSR catalysts on both the catalyst structure and its NO<sub>x</sub> storage capacity. The catalysts used were model catalysts composed of Pt and/or Ba on Al<sub>2</sub>O<sub>3</sub>. For this purpose, the activity of the materials toward NO<sub>x</sub> storage was measured in a fixed bed reactor at 300 °C in the presence and absence of carbon black in the catalytic bed. The effect of aging induced by contact with carbon black on catalyst NO<sub>x</sub> storage capacity was studied. TEM characterization was also performed.

## 2. Experimental

### 2.1. Materials preparation

The 2 wt.%Pt/γ-Al<sub>2</sub>O<sub>3</sub> (noted Pt/Al<sub>2</sub>O<sub>3</sub>) and 20 wt.%BaO/γ-Al<sub>2</sub>O<sub>3</sub> (noted Ba/Al<sub>2</sub>O<sub>3</sub>) catalysts were prepared by wet impregnation of alumina (Alfa Aesar, 220 m<sup>2</sup>/g) with a solution of platinum (II) acetylacetonate (Alfa Aesar, Pt 48% min) (8.2 g/L in ethanol 4 vol/dichloromethane 1 vol) or an aqueous solution of barium nitrate (Fluka, 99% purity) (70 g/L), respectively. The preparation of the 2%Pt–20%BaO/γ-Al<sub>2</sub>O<sub>3</sub> (noted Pt–Ba/Al<sub>2</sub>O<sub>3</sub>) catalyst involve the impregnation of alumina with the barium nitrate solution then with the platinum acetylacetonate solution. After drying in air at 383 K during 14 h, the catalysts were calcined at 973 K for 2 h under 20% b.v. O<sub>2</sub> in N<sub>2</sub>.

A commercial carbon black (CB), Vulcan 6 from Cabot with a specific surface area equal to 106 m<sup>2</sup>/g, was used as a model for soot particles.

### 2.2. Reactivity tests

The catalytic activity of the different catalysts for NO<sub>x</sub> adsorption and carbon oxidation was measured using a fixed bed quartz reactor (internal diameter 16 mm) placed in the experimental set up described in Ref. [18]. Catalytic tests were performed either with pure catalyst or in the presence of a carbon–catalyst mixture. Catalytic tests with pure catalyst were carried out on a sample of 1.2 g in the reactor. For the experiments performed in the presence of the carbon–catalyst mixture, 200 mg of carbon black, prepared as described in [18], was physically mixed with 1.2 g of catalyst with

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