

Observations on the Aging Environment Dependent NO Oxidation Activity of Model Pt/Al₂O₃ Diesel Oxidation Catalyst

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Abstract The influence of aging environment of model diesel oxidation catalyst Pt/Al₂O₃ on the NO oxidation activity is studied. The fresh catalyst Pt/Al/F (calcined in air at 500 °C) is aged with or without phosphorus (P) poisoning (7.5 wt%) at 800 °C either in air (P/Pt/Al/O or Pt/Al/O) or in simulated diesel exhaust (P/Pt/Al/R or Pt/Al/R). Catalyst aged under diesel exhaust environment (Pt/Al/R) surprisingly presents the best NO oxidation activity under excess of O₂ followed by the fresh (Pt/Al/F) and thermally aged (Pt/Al/O) catalysts. The activity difference between the catalysts is quite large, especially between Pt/Al/R and Pt/Al/O that are aged at the same temperatures but under different environments suggesting the importance of the aging environment for the catalytic activity. The NO oxidation activity of P poisoned catalysts P/Pt/Al/R and P/Pt/Al/O is minute as compared to their P free counter parts indicating that chemical aging is more detrimental for catalytic efficiency than thermal aging.

Keywords Diesel oxidation catalyst · Aging environment · Thermal aging · Chemical aging · Phosphorus · NO oxidation activity

1 Introduction

Diesel oxidation catalyst (DOC) comprising of Pt supported on Al₂O₃ is typically used in combination with a diesel particulate filter (DPF) and NO_x storage reduction (NSR) or selective catalytic reduction of NO_x (SCR) catalyst to mitigate NO_x emissions from lean burn diesel engines. In this system, the efficiency and durability of DOC is the key as it catalyzes NO oxidation reaction that affects the rate and selectivity of NO_x reduction in SCR, NO_x storage capacity in NSR and passive regeneration of DPF by NO₂ [1]. Therefore, the role of different factors such as aging (thermal and chemical) and Pt particle size and shape on the DOC performance has been a topic of research [1–10].

On the one hand, thermal aging, due to high temperature excursions in the DOC monolith, sinters Pt nanoparticles and support as well as wash coat material. On the other hand, chemical aging caused by contaminants like phosphorus (P) interacting with the support, wash coat and Pt nanoparticles leads to occlusion of surface Pt sites. These two aging effects give rise to decreased catalytic efficiency [7–11]. Previous studies on a real DOC monolith of a heavy duty small truck diesel engine aged for 250 h under different driving profiles have shown that chemical contaminants P and Zn originating from the anti-wear and engine oil additives like zinc-dialkyldithiophosphates (ZDDP) deposit heavily with time on DOC [10]. It was also observed that there is a concentration gradient of P, besides temperature gradients, along the DOC monolith. The highest P concentration is at the inlet region (close to the engine) of DOC and it decreases along the length. Consequently, the aged DOC shows decreased catalytic efficiency for oxidation and reduction reactions (under total diesel exhaust composition) as compared to that of fresh

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DOC. However, the role of concentration and temperature gradients along the DOC during the aging process on the NO oxidation activity (under excess O₂) of Pt/Al₂O₃ is not known. In this work, we have studied the influence of aging environments of model DOC Pt/Al₂O₃ on NO oxidation (under excess of O₂) by mimicking the aging process of a real DOC monolith. The results demonstrate that the aging environment affects the NO oxidation activity of the catalysts.

2 Experimental

2.1 Catalysts and Aging Procedure

2 wt% Pt/Al₂O₃ powder (a model DOC) was kindly provided by Umicore AG. The catalyst was calcined in air at 500 °C for 4 h, labelled as Pt/Al/F. The fresh catalyst was then thermally aged in a muffle furnace flowing air at 800 °C for 5 h (denoted as Pt/Al/O). A portion of fresh catalyst was also treated in a plug-flow reactor under simulated lean diesel exhaust gas mixture (feed composition: 3,000 ppm CO, 250 ppm NO, 1,200 ppm C₃H₆, 300 ppm C₃H₈, 11 vol% O₂, 25 vol% CO₂ in N₂) with a flow rate of 200 ml/min at 800 °C for 5 h (labelled as Pt/Al/R). To study the influence of chemical contaminants namely phosphorus (P) on DOC performance, the fresh catalyst powder was impregnated with (NH₄)₃PO₄ and dried at 120 °C over-night. Then, it was either thermally aged in a muffle furnace in air (P/Pt/Al/O) or in a plug-flow reactor under simulated exhaust gas atmosphere at 800 °C for 5 h (P/Pt/Al/R). The phosphorous content was determined to be 7.5 wt% P by Energy Dispersive X-ray analysis. The catalysts were characterized by N₂-physisorption at –196 °C using a Micromeritics ASAP 2020c instrument. Prior to the experiments, the catalysts were pretreated at 350 °C for 2 h. The total surface area and pore volume of the catalysts were determined by the BET method and BJH desorption isotherm, respectively (Table 1).

Table 1 N₂-physisorption data of the catalysts

Catalysts	S _{BET} (m ² /g) ^a	V _{Total} (cm ³ /g) ^b
Pt/Al/F	140	0.47
Pt/Al/O	133	0.47
Pt/Al/R	138	0.47
P/Pt/Al/O	70	0.27
P/Pt/Al/R	55	0.19

^a BET method

^b Based on BJH desorption isotherm

2.2 Activity Tests

NO oxidation activity was determined in a quartz tube reactor (12 mm internal diameter and 400 mm length). The reactor was loaded with 50 mg of catalyst (sieve fraction of 150–200 μm) diluted with quartz particles of the same size. Prior to the reaction, catalysts were pretreated at 300 °C in a flow of 10 vol% O₂ in N₂ for 1 h and subsequently cooled to 50 °C. Then, the reaction mixture (400 ppm NO, 10 vol% O₂, balance N₂ at 700 ml/min) was introduced at GHSV = 92,840 h⁻¹. Product evolution was followed by FTIR (Thermo Nicolet 5700 equipped with an Axiom gas cell).

3 Results and Discussion

N₂-physisorption data of the catalysts Pt/Al/F, Pt/Al/O and Pt/Al/R show comparable surface area and pore volume suggesting that high temperature treatment either in air or in lean exhaust environment does virtually not affect the physical and textural properties of the support alumina of the catalysts (Table 1). However, P poisoned catalysts P/Pt/Al/O and P/Pt/Al/R show dramatic loss in both surface area and pore volume as compared to their P free counter parts Pt/Al/O and Pt/Al/R, respectively. These results indicate that P is located on the surface and within the pores of the support alumina. Also, a fraction of P might be deposited on the surface of Pt nanoparticles [10, 11].

The effect of aging environment of the catalysts on their NO oxidation activity under excess O₂ is shown in Fig. 1. NO oxidation is thermodynamically limited above 350 °C (equilibrium between NO and NO₂) and is kinetically controlled at lower temperatures, which are prominently seen in Fig. 1a. Kinetically controlled low temperature NO conversion is indeed dependent on the catalyst (Fig. 1b), whereas the equilibrium limited high temperature (especially ≥400 °C) NO conversion profiles are independent of the catalyst employed due to reverse decomposition of the product NO₂ into NO and O [12]. Accordingly, the oxidation activity of the catalysts below 300 °C is as follows: Pt/Al/R > Pt/Al/F > Pt/Al/O > P/Pt/Al/R > P/Pt/Al/O.

Astonishingly, catalyst Pt/Al/R aged under lean exhaust environment exhibits the best NO oxidation activity followed by the fresh Pt/Al/F and thermally aged Pt/Al/O catalysts. This activity behaviour is intriguing and is not following the literature that report increased NO oxidation activity with increased Pt particle size. For example, NO oxidation activity (turnover rates) increased by a factor of 100 on increase of Pt particle size from ca. 1.2 to 23 nm on Al₂O₃ [4]. Similarly, 4 times increased activity was also observed on increase in the size of Pt particles from 2.4 to 7 nm supported on Al₂O₃ [13]. According to these results, Pt/Al/R and Pt/Al/O that are aged at 800 °C should in

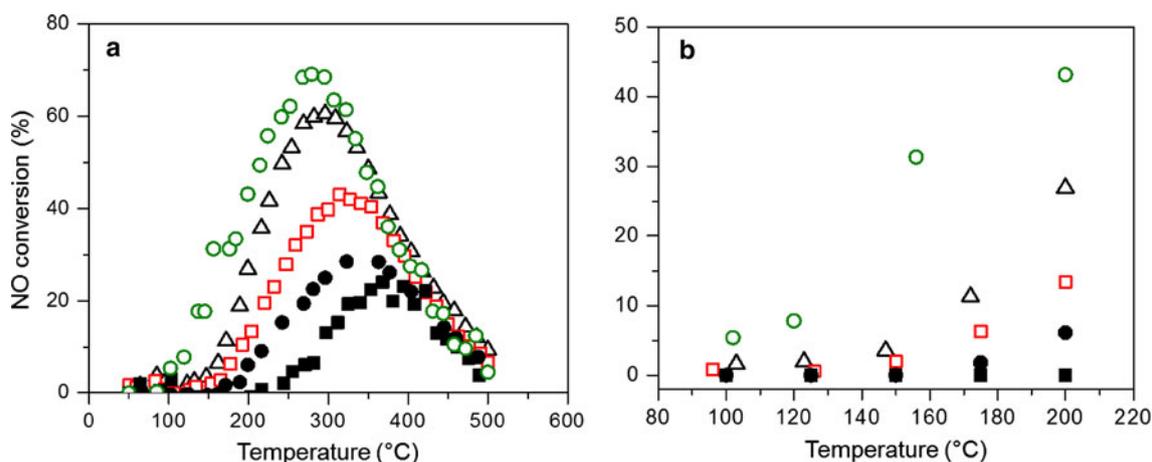


Fig. 1 NO conversion profiles over the catalysts (a): Pt/Al/F (triangle), Pt/Al/R (unfilled circle), Pt/Al/O (square), P/Pt/Al/R (filled circle), and P/Pt/Al/O (filled square). Magnified low temperature activity data of the catalysts (b). Reaction conditions as described in Sect. 2.2

principle present comparable NO oxidation activity and their activity should be better than the fresh catalyst Pt/Al/F that is subjected to calcination only at 500 °C. Moreover, the activity difference between the catalysts Pt/Al/R and Pt/Al/O is quite large (see Fig. 1b). For instance, Pt/Al/R is ca. 15 times more active than Pt/Al/O at 150 °C. At this temperature, the fresh catalyst Pt/Al/F may contain an average Pt particle size of around 4 nm (similar to that on a new DOC monolith [10]) and is ca. 2 times more active than the thermally aged catalyst Pt/Al/O which presumably contains larger Pt particles [10]. Therefore, the activity behavior of the catalysts Pt/Al/R, Pt/Al/F and Pt/Al/O cannot be simply explained by Pt particle size dependence as reported previously [4, 13], indicating the involvement of another factor in the activity determination. Besides agglomeration of Pt particles during the high temperature aging, there might plausibly be another important process occurring during aging that may be governed by the aging environment, for example Pt particle morphology [10, 14]. As a result of this the intrinsic electronic, geometric and catalytic properties of surface Pt sites of Pt nanoparticles evolved under these aging environments vary to different degrees in the catalysts. Hence, the catalysts exhibit significant activity differences.

By comparison of Pt/Al/R and Pt/Al/O with the P poisoned catalysts P/Pt/Al/R and P/Pt/Al/O, it is evident that the latter two show very poor NO oxidation activity (Fig. 1). Between these two catalysts, the P/Pt/Al/R exhibits better NO oxidation activity than P/Pt/Al/O. This activity trend is similar to the corresponding P free catalysts, again indicating the significant role of the aging environment in the activity determination. However, the poor performance of P/Pt/Al/R and P/Pt/Al/O can be due to P that might be interacting with the support and Pt nanoparticles. The interaction can modify the physico-chemical

properties of the support as evident by N₂-physisorption data, for example by forming AlPO₄ like species [11]. This could change the local chemical environment of Pt nanoparticles, also P may perhaps occlude a fraction of surface Pt sites [11]. Consequently, chemical aging caused by P becomes more detrimental for NO oxidation activity than simple thermal aging, in agreement with our previous results reported on Pd/Al₂O₃ based three-way catalysts for CNG vehicle applications [11].

By comparison of the results with the real DOC monolith reported in [10] (as discussed in Sect. 1), it can be suggested that inlet (DOC_{in}), middle (DOC_{mid}) and outlet (DOC_{out}) regions of the DOC monolith experience different aging environments. The DOC_{in} and DOC_{out} regions experience chemical and thermal aging, respectively. Whereas, aging environment at the DOC_{mid} can be unique as it comprises of both exhaust pollutants (propene, propane, CO, CO₂, NO and O₂) and their products such as unburned hydrocarbons, CO₂, H₂, NO₂. It almost excludes chemical contaminants (such as P, Zn). The aging environment along the DOC monolith is similar to that of model catalysts P/Pt/Al/R, Pt/Al/R and Pt/Al/O which represent DOC_{in}, DOC_{mid} and DOC_{out}, respectively. The NO conversion efficiency (at ca. 238 °C under simulated diesel exhaust environment as reported in [10]) of these three regions of the DOC is compared with the corresponding NO oxidation activity of the model catalysts in Fig. 2. Note that the comparison should be treated with caution and is only qualitative due to differences in the reaction conditions. Having said that, the activity trend of DOC_{in}, DOC_{mid} and DOC_{out} coincides well with the corresponding model catalysts as shown in Fig. 2. DOC_{mid} exhibits the best NO conversion efficiency followed by the DOC_{out} and DOC_{in} which correspond to Pt/Al/R, Pt/Al/O and P/Pt/Al/R, respectively. These results confirm that the

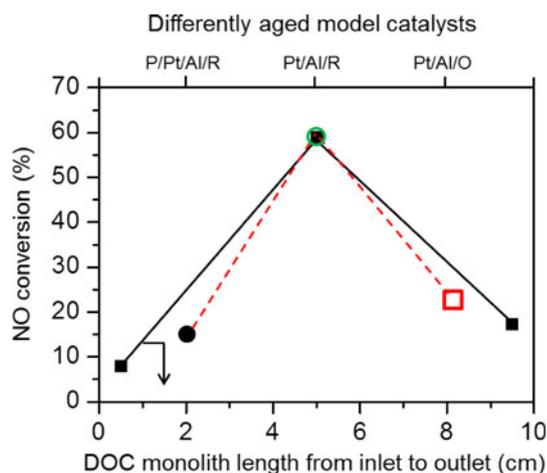


Fig. 2 NO conversion efficiency at 238 °C of the DOC monolith along the length (10 cm in length and 20 cm in diameter) is compared with the corresponding model catalysts (data taken at 238 °C from Fig. 1). DOC samples were taken at different length positions of the monolith. The DOC monolith was aged on a heavy duty small truck engine for 250 h under different driving profiles. Reaction conditions for the DOC samples are reported in [10]

aging environment does play an important role in the catalyst activation and deactivation, further characterization and kinetic studies are in progress to address the role.

4 Conclusions

The effect of aging environment of model DOC Pt/Al₂O₃ on NO oxidation under excess O₂ is studied by mimicking the aging process of a real DOC monolith. The preliminary results show that the aging environment affects significantly the NO oxidation activity of the catalysts. The catalyst aged under diesel exhaust environment at 800 °C

presents the best NO oxidation activity followed by the fresh (calcined at 500 °C) and thermally aged (in air at 800 °C) catalyst. Chemical aging caused by phosphorus can be more detrimental than the thermal aging. The activity trend of the catalysts coincides well with that of an aged real DOC monolith performance that varied along the DOC length, confirming the aging environment dependent NO oxidation efficiency of the catalysts.

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