

## Comparison of O<sub>2</sub> and NO<sub>2</sub> impact on PtO<sub>x</sub> and PdO<sub>x</sub> formation in diesel oxidation catalysts

Panagiotis Boutikos<sup>\*</sup>, Adéla Buzková Arvajová, Jan Březina, Petr Kočí

University of Chemistry and Technology, Prague, Department of Chemical Engineering,  
Technická 5, 166 28 Prague, Czech Republic

<sup>\*</sup>Corresponding author: panagiob@vscht.cz

### Highlights

- Quantification of O<sub>2</sub> and NO<sub>2</sub> activity in PtO<sub>x</sub> and PdO<sub>x</sub> formation.
- Comparison of Pt/Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> catalysts.
- Reaction kinetics model for PtO<sub>x</sub> and PdO<sub>x</sub> formation and their reduction by CO and C<sub>3</sub>H<sub>6</sub>.
- Impact on NO oxidation activity and NO<sub>2</sub> yield in Diesel oxidation catalyst.

### 1. Introduction

The catalytic oxidation of NO to NO<sub>2</sub> in a diesel oxidation catalyst (DOC) is a key step in automotive exhaust gas aftertreatment systems, like NO<sub>x</sub> storage reduction (NSR), the selective catalytic reduction by NH<sub>3</sub> (SCR) and diesel particulate filters (DPFs) [1, 2]. Hence, it is desirable to control the NO oxidation activity of DOC and maintain it at a proper level.

In several experimental studies [1,2,3,4], deactivation effects during NO oxidation have been reported. This change in catalytic activity can be attributed to the formation of platinum oxides (PtO<sub>x</sub>), which are less active for the NO oxidation compared to Pt [1]. The PtO<sub>x</sub> formation is induced not only by O<sub>2</sub>, but also by NO<sub>2</sub>, but no systematic experiments comparing the individual contribution of these two oxidative species have been available. PtO<sub>x</sub> decomposes above 400 °C and it can be reduced at low temperatures by NH<sub>3</sub> or NO. Recently, Arvajová et al. reported that it is possible to reactivate the catalyst and increase the NO<sub>2</sub> yield by CO and C<sub>3</sub>H<sub>6</sub> pulses, while keeping overall lean composition of exhaust gas that is natural for Diesel engines [4].

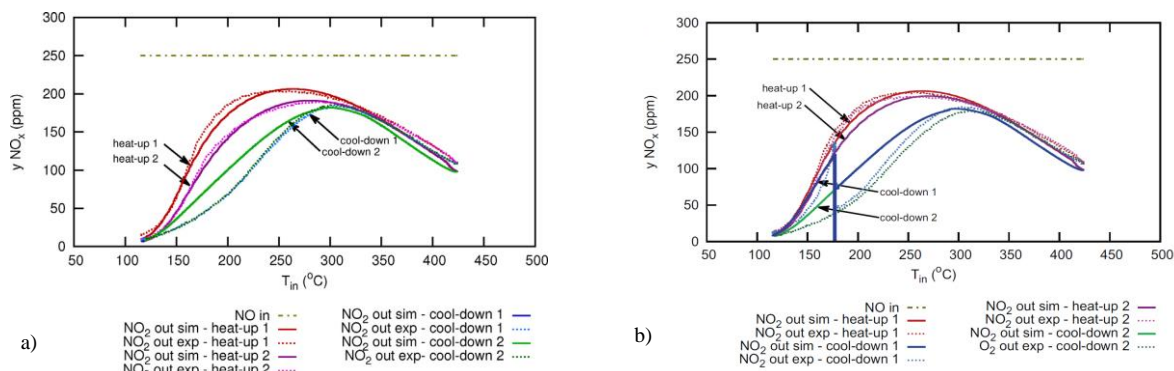
The aim of this work is to compare the impact of O<sub>2</sub> and NO<sub>2</sub> on the PtO<sub>x</sub> and PdO<sub>x</sub> formation during the NO oxidation on Pt/Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> diesel oxidation catalysts and to develop the global kinetic model for the above-mentioned processes on both types of the catalysts.

### 2. Methods

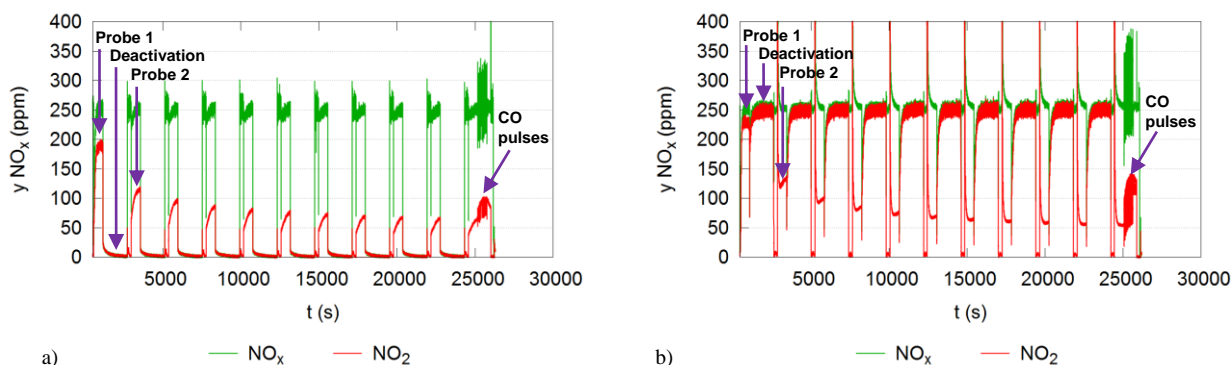
Model diesel oxidation catalysts, Pt/Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> coated on 400 cpsi cordierite monolith, were used for the experimental study. Before each experiment, the catalyst was pretreated in a reductive atmosphere of 2% H<sub>2</sub> in N<sub>2</sub> at 400 °C for 15 min to reduce all Pt or Pd sites to the metallic state. Repeated heat-up and cool-down temperature ramps in the range of 100–400 °C and isothermal deactivation-reativation experiments at 150, 175 and 200 °C with NO oxidation as probe reaction were carried out in a bench flow reactor with defined mixtures of synthetic gases corresponding to Diesel exhaust and GHSV of 60 000 h<sup>-1</sup>.

### 3. Results and discussion

Fig. 1a shows the comparison between the experimental and simulated outlet NO<sub>2</sub> concentration during NO oxidation in subsequent heating and cooling temperature ramps in the case of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. At the beginning, the catalytic surface is fully reduced so that the initial NO oxidation activity during the first heat-up ramp is high. Much lower NO<sub>2</sub> concentration is observed during the following cool-down ramp due to the formation of PtO<sub>x</sub> species in the catalytic surface. The catalyst activity during the second heat-up is still lower than during the first one, indicating incomplete PtO<sub>x</sub> reduction by NO at low temperature. Similar experiments were then performed with a reactivation period, consisting of short lean CO pulses applied at constant temperature (180 °C) during the first cool-down period (Fig. 1b). After the CO pulsation, PtO<sub>x</sub> is almost completely reduced and much higher NO<sub>2</sub> yield is observed in both experiment and simulation.



**Figure 1.** Experimental and simulated NO<sub>2</sub> concentration during NO oxidation subsequent temperature ramps (feed: 250 ppm NO, 8% O<sub>2</sub>, 8%CO<sub>2</sub>, 8%H<sub>2</sub>O) (a) without and (b) with CO pulses (1000 ppm CO).



**Figure 2.** Isothermal experiment at 200°C with alternated probe periods of NO oxidation and deactivation periods with (a) 8% O<sub>2</sub> and (b) 250 ppm NO<sub>2</sub>, followed by CO pulsation. Probe feed: 250 ppm NO, 8% O<sub>2</sub>, 7%CO<sub>2</sub>, 7%H<sub>2</sub>O + 1000 ppm CO pulses.

Fig. 2 shows isothermal PtO<sub>x</sub> formation experiments at 200°C. The Pt/Al<sub>2</sub>O<sub>3</sub> oxidation can be induced either by O<sub>2</sub> (Fig. 2a) or NO<sub>2</sub> (Fig. 2b). Initially, the catalyst is fully reduced so that during the first probe period of NO oxidation the highest NO<sub>2</sub> production is observed. The first probe period is followed by a deactivation period during which Pt oxidation is induced by O<sub>2</sub> (Fig. 2a) or NO<sub>2</sub> (Fig. 2b). The second probe period of NO oxidation after the deactivation then provides a lower NO<sub>2</sub> yield. The probe and deactivation periods are alternated, revealing gradual decrease of NO<sub>2</sub> yield due to PtO<sub>x</sub> formation, until steady state is achieved after 25 000 s (ca. 7 h) of catalyst operation. The PtO<sub>x</sub> is partially reduced during the lean CO pulsation at the end of the experiment with the NO<sub>2</sub> yield being near to that of the second probe period. Similar experiments are performed with the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst and kinetic parameters are compared for both catalyst types.

#### 4. Conclusions

NO<sub>2</sub> exhibits a stronger effect on the Pt oxidation than O<sub>2</sub>. However, due to much higher oxygen concentration present in typical exhaust gas mixture, similar overall rate and extent of deactivation is observed for both oxidizing agents. The catalyst activity can be partly restored by CO or C<sub>3</sub>H<sub>6</sub> pulses while keeping overall lean conditions. The developed kinetic model can be used for the optimization of NO<sub>2</sub> yield in DOC during driving cycles [5].

#### References

- [1] L. Olsson, E. Fridell, J. Catal. 210 (2002), 340–353.
- [2] W. Hauptmann, M. Votsmeier, J. Gieshoff, A. Drochner, H. Vogel, Appl. Catal. B: Environ. 93 (2009), 22–29.
- [3] K. Hauff, U. Tuttlies, G. Eigenberger, U. Nieken, Appl. Catal. B: Environ. 123-124 (2012), 107–116.
- [4] A. Arvajová, P. Kočí, V. Schmeißer, M. Weibel, Appl. Catal. B: Environ. 181 (2016), 644–650.
- [5] A. Arvajová, P. Kočí, Chem. Eng. Sci. 158 (2017), 181–187.

**Keywords:** NO oxidation; reaction kinetics; catalyst reactivation; mathematical modeling.