

## Support effect towards Palladium particles stability followed during NO+H<sub>2</sub>+O<sub>2</sub> reactions: comparison between Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/LaCoO<sub>3</sub> catalysts

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### Introduction

The use of reducible supports has been largely applied on deNO<sub>x</sub> 3-way catalysis. Interesting activities from catalysts using perovskite support were reported from literature for the selective reduction of NO into nitrogen for mobile sources and stationary sources<sup>[1,2]</sup> suggesting that perovskite could be envisaged as an alternative to ceria zirconia supports. Previous studies have evidenced surface and structural changes on Pd-LaCoO<sub>3</sub> systems in the course of the NO+H<sub>2</sub> reaction in excess oxygen<sup>[3]</sup>. In parallel to support reconstruction, the stabilization of oxidic palladium species was characterized by XPS with an unusual binding energy of 337.2 eV after stabilization at high temperature in lean conditions<sup>[3,4]</sup>. This binding energy value was higher than PdO phase (336.2 eV). Uenishi et al<sup>[5]</sup> have proposed the migration of palladium species inside the framework of the perovskite on a LaFe<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub> system after high temperature thermal treatment in oxidizing atmosphere. The possible insertion of palladium inside the framework of our LaCoO<sub>3</sub> catalyst was examined in oxidizing conditions in a temperature range of 25-500°C. Our work was focused on the comparison of Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/LaCoO<sub>3</sub> catalysts during *in situ* reduction and reaction under NO+H<sub>2</sub>+O<sub>2</sub> in *operando* and *in situ* conditions. The influence of the support and metal loading was investigated and characterized with XPS, temperature-programmed reaction and XANES/EXAFS.

### Materials and Methods

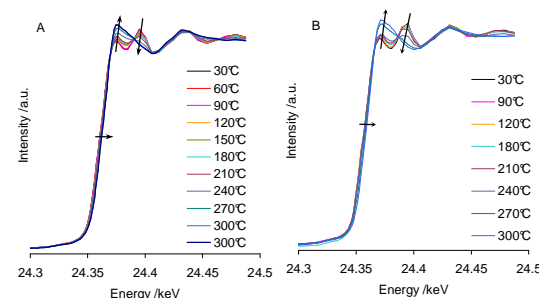
Pd/LaCoO<sub>3</sub> (16 m<sup>2</sup>g<sup>-1</sup>) catalysts were prepared according to a so-called sol-gel method using a citrate route and classical wet impregnation of the palladium precursor. Pd/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared using the same procedure as for the Pd/LaCoO<sub>3</sub> catalysts. Catalysts were finally calcined at 400°C and reduced at 300°C overnight. Alternatively, LaCo<sub>1-x</sub>Pd<sub>x</sub>O<sub>3</sub> samples were prepared by introduction of palladium during a sol-gel synthesis of the perovskite and after calcination at 600°C. Operando EXAFS (Palladium K-edge energy) and *in situ* XPS experiments were used to follow the chemical environment of palladium and its evolution during the 0.1%NO+0.5%H<sub>2</sub>+3%O<sub>2</sub> reaction on 1%Pd-LaCoO<sub>3</sub> and 1%Pd-Al<sub>2</sub>O<sub>3</sub> catalysts. The effluents were analyzed on-line using a  $\mu$ GC chromatograph.

### Results and Discussion

The stabilizing effect of the perovskite support was examined and compared to that of a non-reducible support Al<sub>2</sub>O<sub>3</sub>. After calcination, the binding energy value of Pd 3d photopeak was 336.4 eV and 337.3 eV on Al<sub>2</sub>O<sub>3</sub> and LaCoO<sub>3</sub> respectively evidencing the higher interaction of oxidic palladium species with the perovskite support. The reduction of Pd particles followed with XANES occurred significantly at higher temperature on LaCoO<sub>3</sub> support than on alumina support. During the temperature programmed reaction, the oxidation of Pd particles arose at 90°C and 210°C on Al<sub>2</sub>O<sub>3</sub> and LaCoO<sub>3</sub> respectively as illustrated on XANES spectra (Fig 1). The different behavior of Pd species depending on the support was also examined in EXAFS in terms of the coordination of Palladium atoms. After a 2h steady state at 300°C, the EXAFS spectrum was similar to that of a PdO spectrum with the characteristic coordinations of Pd. At higher temperature and as previously observed on XPS experiments, the chemical environment of Pd seemed to be perturbed after stabilization at 500°C under NO+H<sub>2</sub>+O<sub>2</sub> reaction mixture. These results will be discussed and related to changes in activity and selectivity in the presentation.

### Significance

The use of perovskite and/or palladium in environmental catalysis applications is in the process of development and the characterization of the catalyst during the reaction is an essential point for further improvements and optimizations. This present study reports the support effect on stabilization of palladium as metallic or oxidic particles.



**Figure 1.** XANES spectra of K-edge energy of Pd for Pd/Al<sub>2</sub>O<sub>3</sub> (A) and Pd/LaCoO<sub>3</sub> (B) catalysts during the operando temperature programmed reaction under 0.15%NO+0.5%H<sub>2</sub>+3%O<sub>2</sub>.

### References

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