

# Improved thermal stability of lanthanum-deficient perovskite-based catalysts for the catalytic decomposition of N<sub>2</sub>O from nitric acid plants

Yihao Wu<sup>1</sup>, Xianzhe Ni<sup>1</sup>, Camila Pedraza<sup>1</sup>, Christophe Dujardin<sup>1\*</sup>, Pascal Granger<sup>1</sup>

<sup>1</sup> Université Lille 1, UCCS CNRS, UMR 8181, 59655 Villeneuve d'Ascq Cedex, France

\*corresponding author: christophe.dujardin@univ-lille1.fr

## Introduction

There is a growing interest to minimize the emissions of nitrous oxide (N<sub>2</sub>O) as side-product from nitric acid plants due to a global warming potential of approximately 300 times higher than that of CO<sub>2</sub>. Different strategies have already been implemented at industrial scale but they are still suffering from significant drawbacks essentially associated to a poor selectivity and sometimes a short lifetime in particular when the catalytic process is inserted downstream the ammonia burner. Previous in-situ XRD measurements performed in our laboratory revealed the excellent thermal stability of perovskite based catalysts in the presence of steam at high temperature [1], which suggests its potential application for the decomposition of nitrous oxides from nitric acid plants. X-Ray Photoelectron Spectroscopy measurements usually evidence a surface atomic ratio of Co/La < 1 that could reflect a surface enrichment in Lanthanum. The non-stoichiometric perovskite-based catalysts were examined in order to investigate a possible support effect of segregated oxides on perovskite that could enhance or lower the catalytic activity subsequently. An additional aspect has to be taken into account associated with the catalyst selectivity because the decomposition of NO must be avoided to preserve the cost efficiency of those typical industrial plants.

## Materials and Methods

Stoichiometric and Lanthanum-deficient Perovskite-based catalysts (LaCo<sub>1-y</sub>O<sub>3±λ</sub>, La<sub>1-x</sub>CoO<sub>3±λ</sub>, La<sub>1-x</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3±λ</sub> and La<sub>1-x-y</sub>Ce<sub>y</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3±λ</sub>) were synthesized according to a conventional sol-gel method involving a citrate route [2]. Precursors thus obtained were dried overnight at 80°C then calcined in air at 600°C or 900 °C for 8 h. The prepared catalysts were characterized by BET, XRD, H<sub>2</sub>-TPR and XPS. Temperature-programmed experiments were performed in a fixed-bed flow reactor using 0.7 g of catalyst with a total flow of 15 L.h<sup>-1</sup> within a temperature range between 20 and 900°C. The reactant mixture was typically composed of 0.1 vol.% N<sub>2</sub>O, 5 vol.% NO, 6 vol. % O<sub>2</sub>, 15 vol. % H<sub>2</sub>O and balanced by He. A second catalytic test was performed after ageing overnight at 900°C under reactant mixture in order to characterize the thermal stability of our catalysts in the presence of steam.

## Results and Discussion

The XRD patterns recorded on the catalysts evidence the rhombohedral structure of LaCoO<sub>3</sub> and a slight segregation of La<sub>2</sub>O<sub>3</sub> on LaCo<sub>1-y</sub>O<sub>3±λ</sub> samples that could be related with the increase of specific surface area up to 12 m<sup>2</sup>/g (LaCo<sub>0.8</sub>O<sub>3</sub> calcined at 900°C). In the case of La<sub>1-x</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3±λ</sub> samples, a progressive segregation of cobalt oxide is revealed with decreasing lanthanum stoichiometry but the specific surface area remains almost unaffected. The reducibility of these series of catalysts is examined by using H<sub>2</sub>-temperature-programmed reduction. The typical profile related to H<sub>2</sub> consumption exhibits 2 domains of reduction, the reduction of Co<sup>3+</sup> into Co<sup>2+</sup> around 300-450°C and the subsequent reduction of Co<sup>2+</sup> into Co<sup>0</sup> above 500°C in agreement with H<sub>2</sub> consumption. The modification of stoichiometry slightly changes the reducibility accompanied with a shift of temperature T<sub>max</sub> for both domains. The characterisation of solids clearly evidences the formation of perovskite structure and the segregation of either La<sub>2</sub>O<sub>3</sub> that enhances the specific surface area for LaCo<sub>1-y</sub>O<sub>3±λ</sub> or the

preferential segregation of Co<sub>3</sub>O<sub>4</sub> in the case of La<sub>1-x</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3±λ</sub> solids. We pay a special attention to a possible support effect that could involve the stabilisation of active phase.

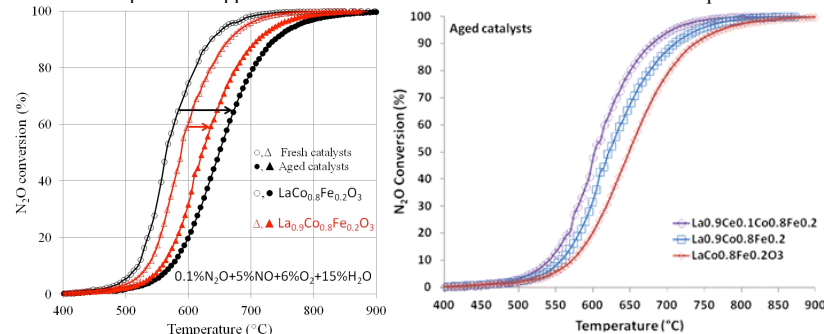


Figure 1: Effect of thermal ageing on catalytic N<sub>2</sub>O decomposition on LaCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3±λ</sub> and La<sub>0.9</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3±λ</sub> catalysts (A) and Comparison of N<sub>2</sub>O conversion curves after ageing thermal treatment of LaCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3±λ</sub>, La<sub>0.9</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3±λ</sub> and La<sub>0.9</sub>Ce<sub>0.1</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3±λ</sub> catalysts (B). Reaction mixture: He+0.1% N<sub>2</sub>O+5% NO+6% O<sub>2</sub>+15% H<sub>2</sub>O

The Figure 1 compares the catalytic activity for the N<sub>2</sub>O decomposition into N<sub>2</sub> for the freshly calcined catalyst and the catalyst aged under reaction conditions at 900°C overnight. It should be noticed that all the samples from these series show an exclusive selectivity towards N<sub>2</sub>O decomposition in N<sub>2</sub> without NO loss. A strong activity enhancement in N<sub>2</sub>O conversion is observed on the substituted sample (LaCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3±λ</sub>) and the introduction of iron on LaCoO<sub>3</sub> leads to a stabilisation of the solid revealed by a decrease of the deactivation after ageing. This synergy effect is correlated to the improvement of oxygen mobility which agrees with the observation of H<sub>2</sub>-TPR. Moreover after ageing procedure, the catalytic activity of La<sub>0.9</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3±λ</sub> and La<sub>0.8</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3±λ</sub> samples remains higher than stoichiometric ones. Higher resistance to deactivation is obtained on La-deficient perovskite solids. Surface reconstruction is evidenced at high temperature in severe reaction conditions. Additional improvement can be obtained by partial substitution of lanthanum in perovskite structure with cerium. The influence of the lanthanum excess at the surface of perovskite solids and improvement through partial substitution as well as lanthanum deficiency will be discussed during the presentation.

## Significance

The thermal stability of perovskite catalysts is a key parameter which can be of great importance for various applications. This study presents a fundamental approach for better understanding of surface reconstruction and influence of surface lanthanum excess towards the catalytic performances.

## Acknowledgements

We gratefully acknowledge the IRENI and the ADEME for financial support through a PhD fellowship (Y. Wu).

## References

1. Y. Wu et al. *Applied Catalysis B* 140–141 (2013) 151–163
2. Y. Wu et al. *Applied Catalysis B* 125 (2012) 149–157