

# Natural Gas Vehicle post-combustion catalysts : How to manage support effect to magnify the performances of noble metals in methane abatement

Amaury Decoster<sup>1</sup>, Fabien Dhainaut<sup>1</sup>, Pascal Granger<sup>\*,1</sup>

<sup>1</sup>Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France

# Significance and Relevance

Nowadays, catalytic end-of-pipe technologies are widespread worldwide. However, important challenges are coming across associated to the transition from liquid fueled engines to gas fueled engines. In the frame of this transition, natural gas can be attractive in terms of carbon footprint and less harmful atmospheric pollutant emissions. Existing catalytic technologies use palladium extensively to remove traces of methane in the exhaust acting as powerful greenhouse gas. The European community classified PGMs as strategically important materials stimulating a strong reduction in their uses. Stabilization/magnification of PGM efficiency thanks to support effect with the use of spinel structure has been evaluated. Better insights into reaction mechanisms driven by the extent of the Pd-support interface can provide useful guidelines to comply with these requirements.

Preferred and 2<sup>nd</sup> choice for the topic: Automotive and stationary emission control and Fundamental advances in understanding catalysis as second choice Preferred presentation: (Oral preferred or Short Oral)

### **Introduction and Motivations**

Nowadays, end-of-pipe catalytic technologies are widespread worldwide. However important challenges are coming across associated to the transition from liquid powered engines to gas powered engines which should lead to further technical adaptations to improve the efficiency of the existing catalytic end-of-pipe technologies.<sup>1</sup> In the frame of this transition, natural gas can be considered much more attractive than diesel and gasoline fueled-engines in terms of reduction of atmospheric pollutant emissions as well as economic terms.<sup>2,3</sup> Presently catalytic after-treatment technologies are intimately related to an extensive use of platinum group metal (PGM) as well as rare earths which have been classified by the European community as strategically important materials for which a reduction in the use is strongly advised. On this basis, new conceptual ideas should emerge that guide innovation in the development of new generations of post-combustion catalysts. Possible alternatives integrating reduction in the use of PGM should obey to specific prerequisites such as : (*i*) the promotion of the dispersion of PGM avoiding strong inhibition effects and structural instabilities (*ii*) the magnification of their intrinsic catalytic properties.

Spinel structures have been developed  $Co_xFe_{4-x}O_4$  further doped with palladium. Their intrinsic catalytic properties are related to the oxidation state of cobalt and the reactivity of lattice oxygen species depending on the Co-O bond strength.<sup>4,5</sup> Both appear as key parameters to activate the C-H bond breaking in CH<sub>4</sub> molecule. Palladium is regarded as a benchmark for methane combustion exceptionally in lean conditions corresponding to the stabilization of PdO. On the other hand, investigations of catalytic performances at high temperature in an oxygen-depleted environment are scarce while important challenges lie in the destabilization of Pd-O leading to unreactive metallic Pd species.<sup>6</sup> Particular attention was paid to the protocol used for Pd incorporation, *i.e.* one pot vs. sequential method that lead to different degree of dispersion and interface. Catalytic performances for the CH<sub>4</sub>/O<sub>2</sub> reaction were evaluated at various richness in the presence and in the absence of water. Thermal aging has been investigated showing that the thermal stability is intimately related to the selected method for Pd incorporation governing the Pd-support interface driving the kinetics of this reaction.



#### **Results and Discussion**

In a first attempt, different cobalt compositions in  $Co_xFe_{3-x}O_4$  mixed oxides were examined showing magnified intrinsic catalytic properties for  $CoFe_2O_4$  pre-reduced in H<sub>2</sub> at 250°C. Pre-reductive treatment showed a complete reduction of  $Co^{3+}$  into  $Co^{2+}$  while  $Fe^{3+}$  valency remains unchanged. Palladium was incorporated by impregnation on calcined samples or during the coprecipitation step according to a *one pot* method corresponding Pd/CoFe<sub>2</sub>O<sub>4</sub> or Pd-CoFe<sub>2</sub>O<sub>4</sub> catalysts respectively. Both were similarly pre-reduced at 250°C before reaction. XRD analysis in Fig .1 reveals a spinodal decomposition process resulting in the coexistence of two spinel structures which differ from their composition. TEM-EDS analysis confirm the presence of Co- and Fe-rich spinel structures. Raman and Mössbauer spectroscopy analyses also show different distributions of Fe<sup>3+</sup> cations in tetrahedral and octahedral symmetry.



**Figure 1.** XRD patterns recorded on one pot  $Pd-Co_2FeO_4$  (a); TEM-EDS analysis recorded on  $Co_2FeO_4$  calcined at 600°C in air (b).

In situ XPS study, carried out on  $Co_2FeO_4$  and doped-Pd  $Co_2FeO_4$  catalysts showed the evolution of the oxidation state of Pd and transition metals after reduction at moderate temperature, *i.e.* 250°C. In situ reduction of undoped-  $Co_2FeO_4$  only involves the reduction of  $Co^{3+}$  into  $Co^{2+}$ . On the other hand, Pd incorporation promotes the reduction of  $Co^{3+}$  and  $Fe^{3+}$  up to the formation of metallic  $Co^0$  and  $Fe^0$ species. It appears that these changes are weakly sensitive to the method use for Pd incorporation.

The kinetics has been investigated in stoichiometric and lean conditions corresponding to  $O_2/CH_4$  ratio of respectively 2 and 20. Reaction rate measurements were discussed and modelled according to two reaction mechanisms involving reactive chemisorbed  $O_*$  species from the dissociative adsorption on palladium or reactive surface lattice 'O' species from the spinel. Both have been equally considered and their contribution has been estimated based on the adjusted kinetic and thermodynamic constants for adsorption. In fact, the richness plays a determining role with the prevalence of surface lattice 'O' species in oxygen depleted environment. Aging leads to controversial observations as for one-pot samples the involvement of surface lattice 'O' species accentuates irrespective of the richness conditions while the reverse tendency affect impregnated samples becoming after aging more sensitive to the reactivity of chemisorbed  $O_*$  species on Pd reflecting a deterioration of the Pd-support interface.

# References

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