

Executive Summary

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Project “Nanoscale perovskite-supported catalysts for the exhaust after-treatment of natural gas vehicles with very low precious metal content“

Natural gas vehicles (NGV) are gaining more and more attention as a serious alternative to conventional gasoline or diesel vehicles: at the end of 2011, there were more than 15 million NGV in use worldwide, this number increasing continuously. Amongst other advantages, NGV have a higher energy efficiency and are fuelled with relatively inexpensive and abundant natural gas (NG). They are also more environment-friendly, as they produce less CO₂ and significantly less NO_x and particulate matter than their gasoline and diesel counterparts. One important drawback, however, is that methane (CH₄), the main component of NG and a potent greenhouse gas, is found in higher concentrations in NGV emissions. As CH₄ is also the most difficult hydrocarbon to oxidize, three-way catalysts (TWC) for NGV are mainly based on Pd, the most active catalyst for CH₄ oxidation, and contain a threefold higher noble metal loading than their gasoline equivalents.

The high temperature (up to 1000°C) and the redox environment of exhaust gases provoke the progressive deactivation of conventional supported noble metal catalysts. This loss of activity, which results from the agglomeration and growth of the active component, is suppressed in so-called ‘self-regenerative’ perovskite-based catalysts. In such materials, a noble metal (e.g. Pd, Pt, Rh) is hosted in a perovskite-type structure (e.g. LaFeO₃, LaAlO₃, CaTiO₃) and can reversibly segregate out (in the form of metal nanoparticles of 1-3 nm) or return to the perovskite lattice (as a metal cation) under reducing or oxidizing environment, respectively. These reversible structural changes, which are fast (only a few seconds at 600°C) and occur even at low temperature (100-400°C), suppress the growth of noble metal particles. Self-regenerative perovskite-based catalysts revealed to be efficient in the treatment of gasoline vehicles and TWCs based on this technology were commercialized in the 2000s in Japan and Europe.

The main objective of this project was to develop a new and efficient perovskite-based catalyst for the treatment of NGV exhausts. As main features, this catalyst should contain a reduced amount of noble metal and exhibit an improved resistance to thermal ageing. Undoped and Pd-doped ABO₃ (A = La, Y, B = Mn, Fe) perovskite-type oxides have been identified as the most promising and were successfully prepared according to different procedures (i.e. amorphous citrate method, ultrasonic spray combustion, solution combustion synthesis, flame spray synthesis), thoroughly characterized and compared.

The synthesis method and the composition of the material greatly influence the coordination state of Pd species. Compared to other one-step preparation procedures, FSS favours the formation of supported Pd nanoparticles which yield much higher CH₄ conversion than Pd ion species incorporated in the perovskite structure. A similar morphology and activity can be obtained by impregnation of Pd on already formed perovskite particles.

YFeO₃ was found to be a choice support for Pd particles as its interaction with the noble metal is too limited to result in the incorporation of Pd in the perovskite structure and still sufficiently strong to considerably limit Pd sintering upon thermal ageing. In fact, moderate sintering of Pd particles is beneficial to CH₄ oxidation activity, therefore indicating that the requirements of gasoline vehicle TWC (high noble metal dispersion which can be maintained through self-regenerative properties) differ from those of NGV TWC. Attempts to increase the activity of Pd/YFeO₃ catalysts by partial substitution at the A- or B-site did not succeed due to the improved solubility of Pd in the substituted oxide supports.

Results obtained on powder samples could be reproduced at the laboratory scale on monolith-supported catalysts. However, engine bench tests showed a much lower activity of the

developed materials. Such differences may be attributed to the presence of catalytic poisons in the real exhaust (water, sulphur) or by the necessity to tune the properties of the catalytic washcoat (e.g. pore volume, pore size) in order to limit mass transfer limitations, which can significantly affect the catalytic performance under high space velocity conditions. Further experiments are needed to better understand these discrepancies.