A joint catalytic and FT-IR spectroscopic study of NO SCR reduction by hydrogen generated in line on perovskite-type catalysts for automotive diesel exhaust gas treatment

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Introduction
Road transport is a major contributor to hydrocarbons (HC), nitrogen oxides (NOx) and particulate matter (PM) emissions in the atmosphere. The prevalent technology available to control NOx emission is indeed the selective catalytic reduction (SCR) by NH3[1].

As an alternative option, the use of CO and light hydrocarbons, already present in the vehicle exhaust or introduced/generated on purpose, has been extensively studied in the seek of alternative reducing agents. More recently, a number of research groups have explored the use of hydrogen as a reducing agent showing a good promise [2]. The high performance of H2-SCR reaction can justify the employment of an on board reformer for H2 generation from diesel oil. In the present paper, the activity of SCS-synthesized perovskite catalysts belonging to the LaFeO3 family was investigated as promoters of the H2-SCR reaction. On the basis of the obtained results, the suitability of the mentioned catalysts for application in the treatment of the diesel exhausts will be finally discussed.

Materials and Methods
A series of perovskite catalysts (LaFeO3, La0.8Sr0.2FeO3, La0.8Sr0.2Fe0.9Pd0.1O3, La0.8Sr0.2Ce0.1FeO3, La0.8Sr0.2Ce0.1Fe0.9Pd0.1O3) was prepared by Solution Combustion Synthesis (SCS) from an aqueous solution of metal nitrates precursors and urea (acting as a sacrificial fuel) and fully characterized by B.E.T., FESEM, XRD and TPD/R/O analyses.

For FT-IR measurements, powders were pressed into self-supporting wafers and outgassed at 150°C or reduced in H2 at 350°C; then, after about 30 mbar of NO were dosed at ca. 170°C on activated samples, FT-IR spectra were recorded at increasing temperatures. The catalytic activity of all prepared materials was performed in a fixed-bed quartz micro reactor under an atmosphere of 1000 ppm NO, 4000 ppm H2, with 5% or without O2, balanced by He, at a rate of 300 ml/min over 100 mg catalyst (W/F = 0.02 g s cm⁻³, GHSV 30,000 h⁻¹). The outlet gas composition was analyzed through NOx/N2O NDIR (ABB) and chemiluminescence NO/NOx (Ecophysics) analyzers vs. the catalyst bed temperature.

The activity tests on powder catalysts show that La0.8Sr0.2Fe0.9Pd0.1O3, exhibits the best activity (T50 ~ 130°C); without oxygen the complete NO conversion to N2 on La0.8Sr0.2Fe0.9Pd0.1O3 occurred at 180-220°C; when oxygen was present, the complete conversion was never reached and nitrogen oxides different from the fed NO were in any case detected. By comparing the activity order of the synthesized catalysts with the TPR curves (figure not showed), a correlation between the level of B site reduction and the activity of the perovskite for NO reduction was pointed out. Adsorption of NO at low temperature on parent LaFeO3 outgassed at 150°C shows the formation of dimeric Fe(NO)2⁺ complexes, with two typical bands at 1760 and 1844 cm⁻¹ [4]; by increasing the temperature, these bands decrease in intensity and, contemporarily, a band forms at 2235 cm⁻¹, due to the formation of Fe(N2O)2⁺ adducts (figure not showed) [4]. After NO adsorption on sample LaFeO3 reduced with pure H2 at 350°C, the same bands form, but the relative intensity of the Fe(N2O)2⁺ adducts is higher, confirming that formation of N2O is favored on the reduced catalyst (figure not showed).

The promising performance of the best catalyst was confirmed also in the structured form without oxygen (T50 ~ 130°C): without oxygen the complete NO conversion to N2 on La0.8Sr0.2Fe0.9Pd0.1O3 occurred at 180-220°C; when oxygen was present, the complete conversion was never reached and nitrogen oxides different from the fed NO were in any case detected. By comparing the activity order of the synthesized catalysts with the TPR curves (figure not showed), a correlation between the level of B site reduction and the activity of the perovskite for NO reduction was pointed out. Adsorption of NO at low temperature on parent LaFeO3 outgassed at 150°C shows the formation of dimeric Fe(NO)2⁺ complexes, with two typical bands at 1760 and 1844 cm⁻¹ [4]; by increasing the temperature, these bands decrease in intensity and, contemporarily, a band forms at 2235 cm⁻¹, due to the formation of Fe(N2O)2⁺ adducts (figure not showed) [4]. After NO adsorption on sample LaFeO3 reduced with pure H2 at 350°C, the same bands form, but the relative intensity of the Fe(N2O)2⁺ adducts is higher, confirming that formation of N2O is favored on the reduced catalyst (figure not showed).

Results and Discussion
The XRD spectra show for all the catalysts synthesized diffraction peaks corresponding to the desired catalysts structure, the FESEM views enlighten the very foam structure, typical of all catalysts synthesized by SCS, then the BET specific surface area (SSA) values range between 3 and 19 m²/g.

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