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

S. Furfori, M. Armandi, B. Bonelli*, N. Russo, D. Fino, G. Saracco, V. Specchia, E. Garrone
Materials Science and Chemical Engineering Department, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129 Torino, Italy;
*debora.fino@polito.it

Introduction

Road transport is a major contributor to hydrocarbons (HC), nitrogen oxides (NO_x) and particulate matter (PM) emissions in the atmosphere. The prevalent technology available to control NO_x emission is indeed the selective catalytic reduction (SCR) by NH_3[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 H_2-SCR reaction can justify the employment of an on board reformer for H_2 generation from diesel oil. In the present paper, the activity of SCS-synthesized perovskite catalysts belonging to the $LaFeO_3$ family was investigated as promoters of the H_2-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 ($LaFeO_3$, $La_{0.8}Sr_{0.2}FeO_3$, $La_{0.8}Sr_{0.2}Fe_{0.9}Pd_{0.1}O_3$, $La_{0.7}Sr_{0.2}Ce_{0.1}FeO_3$, $La_{0.7}Sr_{0.2}Ce_{0.1}Fe_{0.9}Pd_{0.1}O_3$) 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 out gassed at 150°C or reduced in H_2 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 ppmv NO, 4000 ppmv H_2, with 5% or without O_2, 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 NO_x/N_2O NDIR (ABB) and chemiluminescence NO/NO_x (Ecophysics) analyzers vs. the catalyst bed temperature.

The most promising catalyst ($La_{0.8}Sr_{0.2}Fe_{0.9}Pd_{0.1}O_3$) was deposited on a cordierite monolith, coated with γ-alumina (catalyst weight percentage: 15 wt%) [3] and then tested in a lab-scale rig under an atmosphere of 100 ppmv NO, 1000 – 2000 - 4000 ppmv H_2, with and without 5% O_2, balanced by N_2 (GSHV ≈ 30,000 h^{-1}); the outlet gas composition was monitored by the same analytical equipment described above.

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 m^2/g.

The activity tests on powder catalysts show that $La_{0.8}Sr_{0.2}Fe_{0.9}Pd_{0.1}O_3$ exhibits the best activity (T_{50} = 130°C): without oxygen the complete NO conversion to N_2 on $La_{0.8}Sr_{0.2}Fe_{0.9}Pd_{0.1}O_3$ 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_x reduction was pointed out. Adsorption of NO at low temperature on parent $LaFeO_3$ outgassed at 150°C shows the formation of dimeric $Fe(NO)_2^{2+}$ 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 $Fe(N_2O)^{2+}$ adducts (figure not showed) [4]. After NO adsorption on sample $LaFeO_3$ reduced with pure H_2 at 350°C, the same bands form, but the relative intensity of the $Fe(N_2O)^{2+}$ adducts is higher, confirming that formation of N_2O is favored on the reduced catalyst (figure not showed).

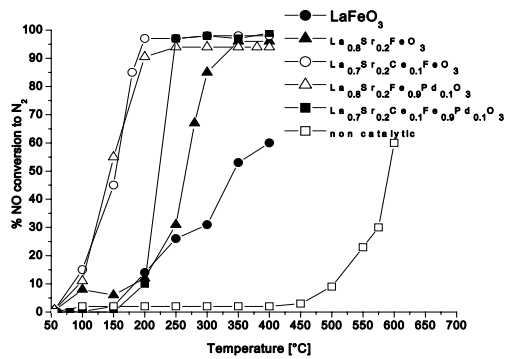

Figure 1. NO conversion to N_2 on powder: 1000 ppm NO, 4000 ppm H_2, GSHV 30000h^{-1}.

The promising performance of the best catalyst was confirmed also in the structured form without oxygen (T_{50} = 130°C; complete conversion at 200 °C); with oxygen (5 vol%), at least a two folds higher hydrogen concentration was required to achieve approximately the same NO to N_2 reduction level obtained with the catalyst in the powder form. In view of a practical application perspective, a further improvement of this performance is needed both in terms of activity and selectivity is being achieved by proper catalyst design.

References

1. Forzatti P. *Appl. Catal. A: General* 222, 221 (2001)
2. Ferri, D., Forni, L., Dekkers, M.A.P., Nieuwenhuys, B.E. *Appl. Catal. B: Environmental* 16, 339 (1998)
3. Civera, A., Pavese, M., Saracco, G., SPecchia, V. *Catal. Today* 83, 199 (2003)
4. Berlier, G., Spoto, G., Bordiga, S., Fisicaro, P., Zecchina, A., Rossetti, I., Selli, E., Forni, L., Gianello, E., Lamberti, C. *J. Catal.* 208, 64 (2002)