After-Treatment of Household Wood-Fired Stove Emissions: from Catalyst Formulation to Full-Scale System

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AFTER-TREATMENT OF HOUSEHOLD WOOD-FIRED STOVE EMISSIONS: FROM CATALYST FORMULATION TO FULL-SCALE SYSTEM

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Abstract

The experimental activity described in this paper is directed to the abatement of the emissions from a wood fired stove for domestic use, and covered the aspects from powder catalyst formulation development to full-scale system implementation. $La_{0.9}Na_{0.1}CrO_3+2wt\%$ Au catalyst was optimized and scaled-up for this application.

Introduction

Pollutant emissions from wood-fired stoves for households are currently the object of an increasing concern: hence, they emit non negligible amounts of wood incomplete combustion products, such as CO, HC and particulate matter (PM). The catalytic abatement of these species is here considered, through the development of appropriate catalytic formulations, and their application in full-scale structured monoliths, to be implemented in real stoves for domestic use.

Stove system set-up

The stove under study in this paper is depicted in Figure 1. The flue gases of the stove chimney were sampled and analyzed (see the heated yellow pipe in Figure 1) in order to characterize the emissions given by wood combustion. Just below the gas sampling pipe, a thermocouple was placed to monitor the temperature, in order to select the appropriate operating window which could be suitable for catalytic conversion of the pollutant species. A specific wood conditioning protocol, before combustion inside the stove, was adopted: the stove was loaded with a beech wood, having an average humidity of 10%, at a nominal load of 7.5 kg in the combustion chamber. Each wood loading cycle (ignition and then depletion) lasts approximately 50-60 min. The gas phase composition was monitored through continuous analysis with a Elsag-Bailey equipment (NDIR for NO, CO, CO_2, SO_2; FID for overall HC; paramagnetic for O_2). The size and number distribution of PM was measured upstream and downstream of the catalytic converter via a TSI Scanning Mobility Particle Sizer (SMPS 3080). Temperature and

Figure 1. Stove system

pollutant emission profiles are shown in Figure 2; PM emissions are later shown in comparison with those downstream of the full-scale catalytic system.
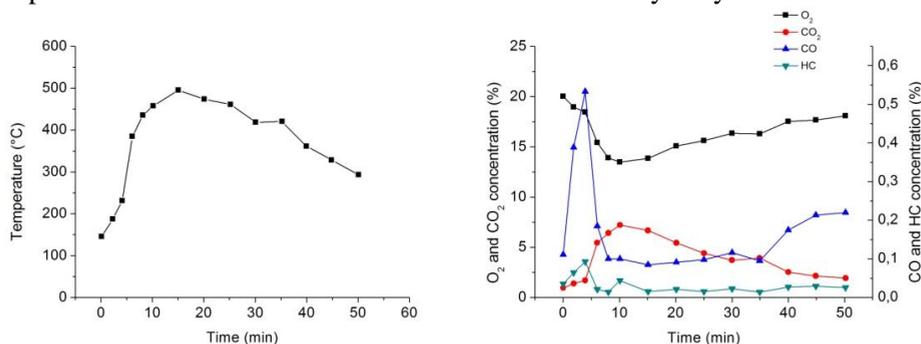
Figure 2. Stove exhaust gases' profiles of temperature and pollutant emissions.

Powder catalyst preparation and testing

A series of La–Cr perovskite catalysts were prepared via a highly exothermic and self-sustaining reaction, the so-called "Solution Combustion Synthesis" method (SCS) [1]. The catalysts were then ground in a ball mill at room temperature, and fully characterized: X-ray diffraction (PW1710Philips) was used to check the achievement of the perovskite oxide structure; field emission scanning electron microscope (FESEM, Leo 50/50 VP Gemini column) was employed to analyze the microstructure of the crystal aggregates of the catalysts as prepared and to assess the size and morphology of the oxide crystals themselves; the specific surface areas of the catalysts were evaluated from BET analysis (Micromeritics ASAP 2010).

The La–Cr perovskite synthesis started from the ABO_3 stoichiometric structure ($LaCrO_3$); then, an A-site sub-stoichiometric $A_{0.9}BO_3$ structure ($La_{0.9}CrO_3$) and two A-site substituted $A_{0.9}A'_{0.1}BO_3$ structures ($La_{0.9}Na_{0.1}CrO_3$ and $La_{0.9}Rb_{0.1}CrO_3$) were synthesized to increment the defective structure of the perovskite.

The activity of the perovskite catalysts was analyzed by means of different techniques. The activity towards carbon monoxide (CO) and unburned hydrocarbons (HC) was assessed by means of temperature programmed oxidation (TPO) which was carried out in a fixed-bed micro-reactor (quartz tube, i.d. 5 mm, placed in an electric oven). The composition of the stove exhaust flue gases, which were measured as described in the former section, was simulated by taking the worse conditions in terms of pollutant concentrations during the testing cycle, in order to be conservative in the estimation of catalyst activity. Therefore, the tested gaseous compositions were the following: 6000 ppm of CO, 10% of O_2 and N_2 as balance, for CO oxidation tests; 1000 ppm of propylene, 10% of O_2 and N_2 as balance, for aliphatic HC oxidation tests; 1000 ppm of benzene, 10% of O_2 and N_2 as balance for aromatic HC oxidation tests. The flow was fed at a constant rate of 50 Nml·min^{-1} (corresponding to a gas hourly space velocity -GHSV- of 12,000 h^{-1}) to the fixed bed which was constituted by 45 mg of powder catalyst and ≈200 mg of inert silica (to act against bed packing, thus minimizing preferential paths and

promoting thermal dilution inside the bed itself). The reaction temperature was controlled through a PID-regulated oven and was varied from 200 to 700 °C at a 5 °C·min^{-1} rate. The outlet gas analysis was performed via NDIR analyzers (ABB).

The activity of the oxidation catalysts towards soot combustion was analyzed by means of temperature programmed combustion (TPC) which was carried out in the same fixed-bed micro-reactor, according to the standard operating procedure described in [2]: a N_2 flow containing 10% of O_2 was fed, at the constant rate of 50 Nml·min^{-1}, to the fixed bed which was constituted by 50 mg of a mixture of carbon and powdered catalyst (1:9 on a mass basis), diluted with ≈200 mg of inert silica. The resulting amounts of each species was the following: 45 g of catalyst, 5 mg of soot, 200 mg of silica. All experiments were performed by using soot sampled from stove emissions.

The $La_{0.9}Na_{0.1}CrO_3$ perovskite, which showed the best activity among the prepared catalysts, was then improved towards CO oxidation by adding a 2wt% of Au [3], which was deposited over pre-formed perovskites via "Incipient Wetness Impregnation" (IWI) by the addition drop-by-drop of an aqueous solution of $HAuCl_4$. The impregnated powders were then dried in an oven at 120°C for 12 h, and finally calcined in air at 500°C for 5 h in order to decompose the salts and obtain small and well dispersed gold clusters over the perovskite surface.

The full set of results of the testing campaign on powder catalysts is gathered in Figure 3. The synthesized perovskites showed BET surfaces between 21.3 and 26.1 m^2/g, which was not the discriminating parameter for catalyst activity ranking.
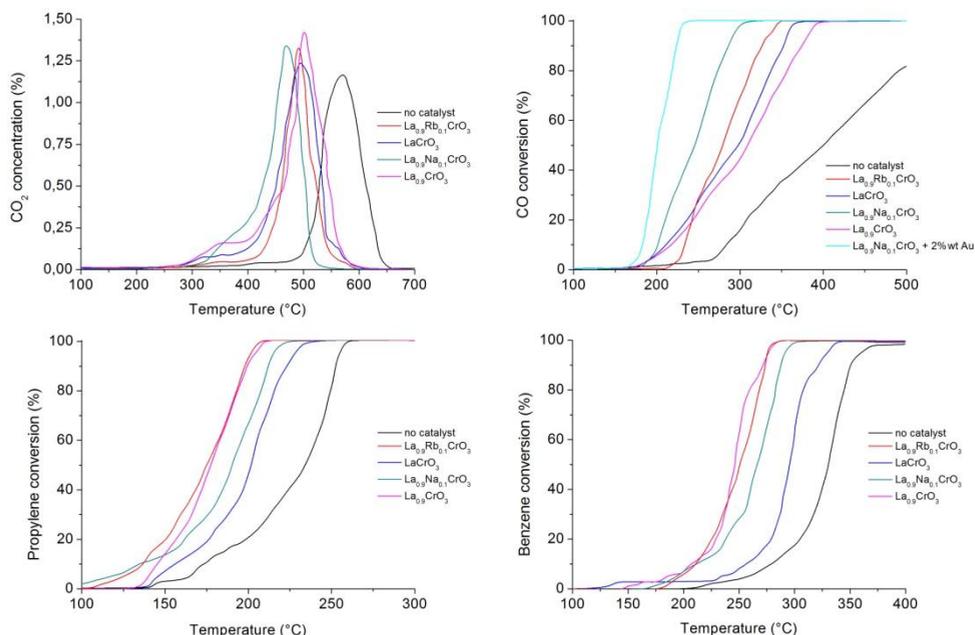
Figure 3. From left to right, and from top to bottom: soot, CO, propylene and benzene oxidation tests (see the text for detailed experimental conditions) with powder catalysts.

The $La_{0.9}Na_{0.1}CrO_3$ perovskite showed the best results among the investigated ones: 100°C reduction of the soot combustion peak T_p (470°C instead of 570°C of the non-catalytic system); 150°C reduction of the CO half conversion temperature T_{50} (250°C instead of 400°C), further reduced with the addition of 2%wt Au (T_{50}=200°C); 40°C reduction of the propylene T_{50} (195°C instead of 235°C); 60°C reduction of the benzene T_{50} (270°C instead of 330°C).

Lab-scale catalyzed monolith preparation and testing
The best perovskite catalyst $La_{0.9}Na_{0.1}CrO_3$, and the Au-improved one, were deposited on a structured support, in order to evaluate the mass transfer effects occurring on catalytically coated flow-through monoliths.
Cordierite honeycombs produced by Chauger (diameter: 34 mm, length: 25 mm, cell density: 200 cpsi) were used: first, a thin layer of γ-alumina (Al_2O_3) was deposited at 5% of the monolith weight, in order to improve the subsequent adhesion of the catalytic powder to the monolith. Then, in order to catalyze the γ-alumina wash-coated monolith with the perovskite, the *in situ* SCS method was used [4]. The specific amount of deposited perovskite was 6wt%, in order to have the same W/F of the powder catalyst tests. Finally, the deposition of 2wt% (based on the perovskite catalyst weight) of Au was again performed by IWI, through monolith dipping into a $HAuCl_4$ solution. An O_2 concentration of 10% and 7%, and the same gaseous pollutant concentration (6000 ppm of CO, 1000 ppm of propylene, 1000 ppm of benzene) were used for CO and HC catalytic abatement assessment. Two gas flow rates were adopted: 1900 l/min, which is equivalent to a GHSV of 3500 h^{-1}, and 5500 l/min (equivalent to 10000 h^{-1}).
The mass transfer effects in the monolith worsened the oxidation capability of the system with respect to the powder catalyst, as can be seen from the shift of CO and propylene total conversion from ≈225°C to above 550°C (at 10000 h^{-1}), for both gaseous species. Benzene total oxidation shifted as well from around 300°C to more than 400°C, regardless of the O_2 concentration. However, the catalytic activity of supported $La_{0.9}Na_{0.1}CrO_3$ + 2wt%Au was still within the observed gaseous emission temperature ranges, therefore being suitable for this application (Figure 4).
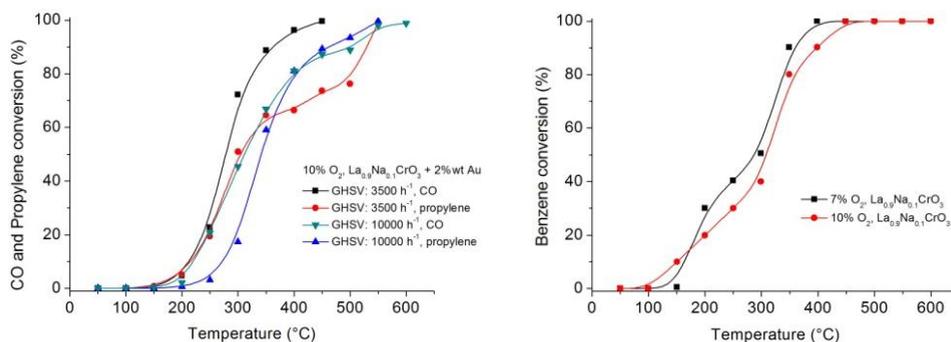

**Figure 4.** CO, propylene and benzene oxidation tests with supported catalysts.

Full-scale catalyzed monolith preparation and testing

The investigation of the most suitable full-scale monolith, to be installed in exiting stoves, was tackled by employing the best catalytic formulation which has been devised in the former steps (powder and lab-scale monolith forms), with the aim to oxidize the emissions from wood incomplete combustion in the stove.

The full-scale tests were aimed to assess the catalyst activity with respect to the wood-loading cycle: both longer exposure times (through a 4-time repetition of the standard 60 min loading cycle) and different wood-loadings (7.5 kg and 3.5 kg, both of beech wood at 10% humidity) were investigated.

The stove was loaded as described in the former section, i.e. with a 15 min heating phase performed with dry wood, followed by a beech (10% humidity) wood-loading at nominal capacity (7.5 kg). The bare monoliths, made of cordierite, were provided by CTI (Céramique Techniques Industrielles), and had the following characteristics: 22 cm in diameter, 8 cm in height, 1820 g in weight, 50 cpsi (cells per square inch), 3 mm of square channel side. The 50 cpsi cell opening demonstrated to be suitable in preventing severe flying ash fouling during our tests. These monoliths were catalyzed with $La_{0.9}Na_{0.1}CrO_3$ and $La_{0.9}Na_{0.1}CrO_3 + 2wt\%$ Au, with a catalyst loading equal to 10% with respect to the monolith weight. The same technique used for lab-scale monolith coating, was employed in this case: *in situ* SCS for perovskite synthesis and IWI for Au subsequent deposition.

The gas phase composition was monitored through continuous analysis with the formerly mentioned Elsag-Bailey equipment, while the size and number distribution of PM was measured both upstream and downstream of the catalytic converter via the SMPS 3080. The soot abatement efficiency, which could be quantified looking at the emissions upstream and downstream of the monolith, is very high as arises from Figure 5, being almost 1. On the other hand, from Figure 6 it can be seen that higher CO conversions than 80%, and HC conversions close to the unity, could be reached with the $La_{0.9}Na_{0.1}CrO_3+2wt\%Au$ based catalytic system. Conversely, the lower temperatures reached in the 3.5 kg wood-loading cycles reduced the catalyst activity towards CO and propylene conversion.
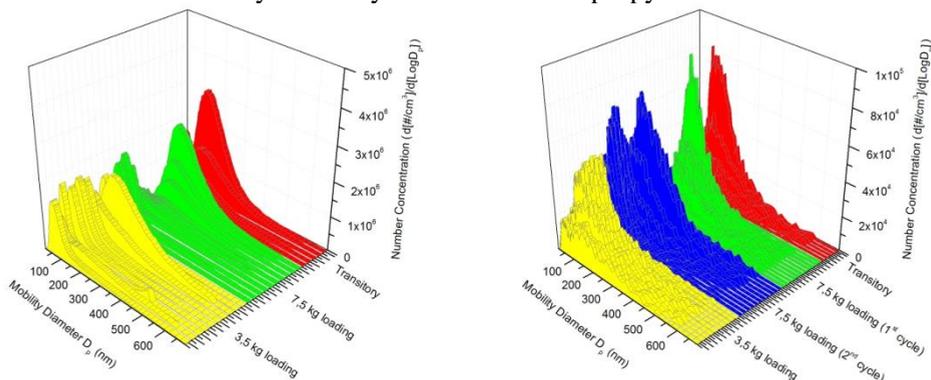
Figure 5. PM emissions up-(left) and down-(right)stream of the full-scale 10wt% catalyzed monolith, for 7.5 and 3.5 kg wood-loadings. Dilution factor ~ 60.
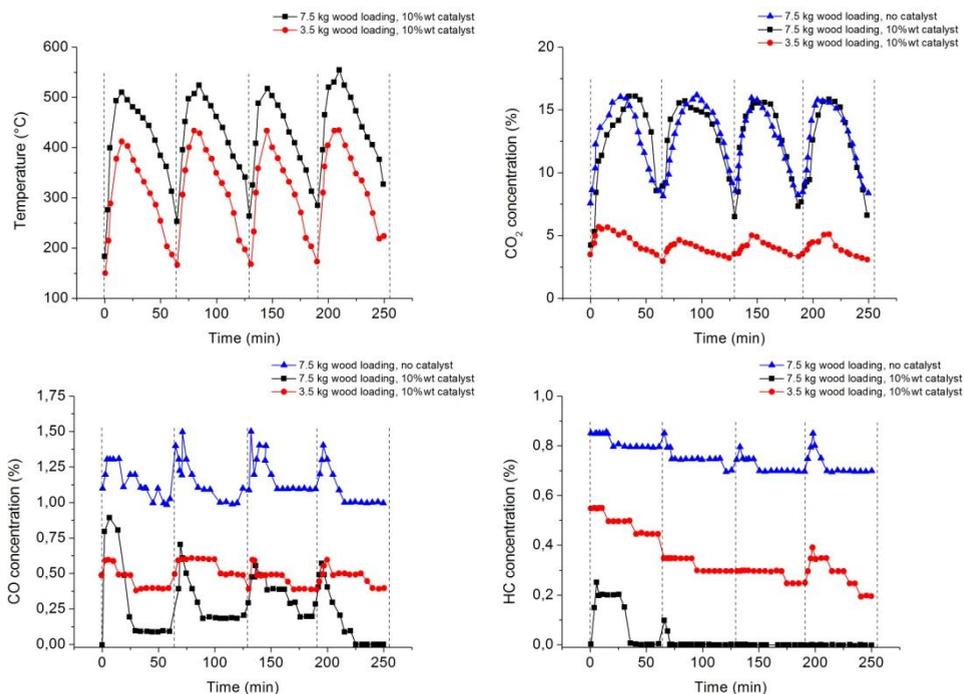
Figure 6. Top: stove operating temperature and CO_2 emissions; bottom: CO and HC oxidation tests with and without the full-scale catalyzed monolith.

Conclusions

$La_{0.9}Na_{0.1}CrO_3$ perovskite catalyst demonstrated to have the overall best activity towards PM, CO and total HC simultaneous abatement. The addition of 2wt% Au further improved CO oxidation. The tests were carried at the worst operating conditions (10% O_2, and even 7% O_2, which are both less than the recorded minimum values), and with different wood-loadings (7.5 kg and 3.5 kg), reaching a catalyst loading of 10wt% (referred to the monolith weight) as the satisfactory and stable (over 4 repeated cycles) configuration for the full-scale catalytic system.

References

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