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Low temperature DPF regeneration by delafossite catalysts

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ABSTRACT

Several Li–Cr delafossite catalysts ($LiCrO_2$, $LiCr_{0.9}O_2$, $LiCr_{0.8}O_2$, $LiCr_{0.7}O_2$, $Li_{0.9}CrO_2$, $Li_{0.8}CrO_2$ and $Li_{0.7}CrO_2$) were prepared via a highly exothermic and self-sustaining reaction, the so-called "solution combustion synthesis (SCS)" method, and characterized by means of XRD, BET, FESEM-EDS, H_2-temperature programmed reduction (TPR) and XPS analyses, as catalysts for the combustion of soot, a major pollutant emitted by diesel engines. These catalysts already showed appreciable activity at 350 °C towards the catalytic combustion of soot even under loose contact conditions. The best prepared catalyst ($LiCr_{0.9}O_2$) could ignite soot combustion well below 350 °C, which is inside the range of temperatures reached at the exhaust line of a diesel engine. The correlation between the activity order and the capability to provide surface adsorbed oxygen (O^-) by the prepared delafossite catalysts, enabled by a shift of the chromium from a high valence to a low valence state, is pointed out as a peculiar feature of these catalysts.

An *in situ* SCS method was tailored to the preparation of a $LiCr_{0.9}O_2$-catalyzed trap based on a SiC wall-flow monolith. Engine bench tests on these catalytic traps (trap loading and regeneration by induced temperature increase) showed that the presence of the catalyst enabled both a more complete regeneration and a one-third fold reduction of the regeneration time compared to the case of a bare, non-catalytic trap. The catalyzed trap was finally characterized in terms of soot emissions during both the loading and the regeneration phase.

1. Introduction

Road transport is a major contributor to the emissions of various greenhouse gases and has significant share in the emission of harmful hydrocarbons, nitrogen oxides (NO_x) and particulate matter (PM). One of the available technologies to control diesel particulate emissions is the use of filters (DPF) to capture soot particles from the exhaust stream [1]. The filter must be regenerated through the combustion of trapped soot in order to prevent engine backpressure increase [2]. Therefore, auxiliary systems are designed to heat the exhaust gases up to the regeneration temperature. The PM combustion temperature can be lowered by using a suitable diesel oxidation catalyst (DOC), thus achieving a valuable fuel saving [3].

In this work, Li–Cr delafossite catalysts were investigated under realistic conditions as catalysts for the combustion of particulate matter. The delafossite-type compounds with general formula $A^+B^{3+}O_2$ have been known and studied for a long time [4] but not as oxidation catalysts to the Authors' knowledge. Their structure can be viewed as the stacking of $[B^{3+}O_2{}^{2-}]_\infty{}^-$ layers made of two closed packed oxygen planes having all octahedral sites occupied by B^{3+} cations, which are connected by planes of A^+ cations arranged according to a triangular network. Each A^+ cation is coordinated linearly to two oxygen anions from the oxygen planes above and below. Depending on the mutual orientations of successive layers, various delafossite structures can exist. In this work, starting from the basic $LiCrO_2$ delafossite catalyst [5], several active catalysts were synthesized via induction of charge deficiency both at the A or B site by forcing local sub-stoichiometries. An analysis of the reaction mechanism, mainly based on both the interpretation of H_2-temperature programmed reaction (TPR) and XPS characterization results, is also provided, which shows the importance of surface adsorbed oxygen species for the soot oxidation activity. Finally, the promising results obtained are verified at a catalytic trap prototype level.

2. Experimental

2.1. Catalyst preparation and characterization

A series of Li–Cr delafossite catalysts were prepared via a highly exothermic and self-sustaining reaction, the so-called "*solution combustion synthesis"* method (SCS) [5]. Particularly, a concentrated aqueous solution of various precursors (metal nitrates and urea) was located in a oven at 600 °C for a few minutes in a crucible, so as to ignite the very fast reaction. Under these conditions nucleation of metal oxide crystals is induced, their growth is limited and nano-

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sized grains can be obtained with large specific volume and surface area.

The catalysts were then ground in a ball mill at room temperature, and fully characterized: X-ray diffraction (PW 1710 Philips diffractometer) was used to check the achievement of the delafossite oxides structure; Field Emission Scanning Electron Microscope (FESEM – Leo 50/50 VP with 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 prepared catalysts were evaluated from BET analysis, using a Micromeritics ASAP 2010 analyzer. As a further characterization procedure, temperature programmed reduction (TPR) experiments were performed on the catalysts in a Thermoquest TPD/R/O 1100 analyser: prior to each run, the catalyst was heated under an O_2 flow (40 ml/min) up to 750 °C. After 30 min stay in O_2 flow at this temperature, the reactor temperature was lowered down to the ambient conditions by keeping the same flow rate of oxygen, thereby allowing complete oxygen adsorption over the catalyst. Afterwards, He was fed to the reactor at 10 ml/min flow rate and kept up for 1 h at room temperature in order to purge out any excess oxygen molecule. After the above pre-treatment, the sample was reduced with a 4.95% H_2/Ar mixture (10 Nml/min) as it was heated at a rate of 10 °C/min. The amount of converted H_2 was monitored via the TCD detector.

X-ray photoelectron spectroscopy (XPS) was used to characterize the surface composition of some selected delafossite-based catalysts: the basic $LiCrO_2$ delafossite and the most active among the developed catalysts. The XPS analyses were carried out with a VG Escalab 200-C X-ray photoelectron spectrometer and a non-monochromatic Mg-K_α source. A pass energy of 20 eV, a resolution of 1.1 eV, and a step of 0.2 eV were used for high-resolution spectra. The effects of sample charging by referring the spectral line shift to the C 1s binding energy value of 284.6 eV were eliminated. This XPS apparatus could also provide a quantitative analysis of the catalyst surface composition. For this purpose, the areas below the XPS peaks were determined with the software ECLIPSE v3.1 VG Scientific using the peak fitting techniques for the O 1s region; peaks area were then normalized, with the Shirley background and the Scofield sensibility factors taken into account.

2.2. Catalytic activity assessment

The activity of the prepared catalysts towards soot combustion was analyzed by temperature programmed combustion (TPC) carried out in a fixed-bed micro-reactor, according to the standard operating procedures described in detail, see [6]: air was fed at the constant rate of 50 Nml/min to the fixed bed constituted of a mixture of carbon and powdered catalyst (1:9 mass basis). All experiments were performed by using, instead of real diesel soot, an amorphous carbon by Cabot Ltd. (particle average diameter: 45 nm in diameter; BET specific surface area: 200 m^2/g; ashes content after calcination at 800 °C: 0.34%; adsorbed water moisture at room temperature: 12.2 wt%; no adsorbed hydrocarbons and sulphates). This condition is conservative because amorphous carbon is more difficult to burn than real diesel soot. The *loose contact* catalyst–carbon mixture was prepared by gentle shaking it in a polyethylene vessel for 1 h. As mentioned above, loose-contact is representative of the real contact conditions occurring in a catalytic trap for diesel particulate removal [7]. The reaction temperature was controlled through a PID-regulated oven and varied from 200 to 700 °C at a 5 °C/min rate. The analysis of the outlet gas was performed via NDIR analyzers (ABB). The peak temperature T_p of the TPC plot of the outlet CO_2 concentration was taken as an index of the catalytic activity. In order to better discriminate the intrinsic catalytic activity of the prepared catalysts the onset ($T_{5\%}$) combustion temperature, defined as the temperature at which 5% of the initial soot is converted, was also considered. In fact, the on-set combustion temperature depends only on the catalytic reaction, in a reaction rate limited regime; whereas, at higher conversion degrees, other phenomena (for instance, mass transfer limitations) could shade the real hierarchy among catalysts.

In order to test the stability of the synthesize catalysts, an aging protocol was carried out by exposing the fresh powder to an atmosphere containing $10\%_{vol}$ of steam and 500 ppm of SO_2 in air, for 6 h at 800 °C. The TPC run and the BET test were then repeated, in order to estimate the loss in specific surface area and the decrease in the soot combustion catalytic activity.

2.3. Catalytic monolith preparation, characterization and activity assessment

The $LiCr_{0.9}O_2$ catalyst, which showed the best activity among the prepared catalysts, was deposited by the *in situ* SCS method [8] directly over the wall-flow filter. The ceramic support was dipped in the aqueous solution of the precursors and then placed into an oven at 600 °C. The aqueous phase was rapidly brought to boil, the precursors mixture ignited and the synthesis reaction took place *in situ*. The support selected was a silicon carbide (SiC) filter produced by NGK (cell structure = 17/200, side = 35 mm, length = 254 mm; pore diameter of channel walls = 23 μm, porosity of channel walls = 52%) which was found to be chemically compatible with the selected catalyst. The load of deposited catalyst was assessed by gravimetric analysis. The specific amount of delafossite deposited was 4.8 wt%. The morphology of the deposited catalyst layer was analysed by FESEM observation, whereas catalyst adhesion to the monolith was assessed by a tailored ultrasonic bath test procedure. The developed trap was tested over real Diesel exhaust gases by means of a simulating light duty vehicle (Iveco F1C Unijet 4 cyl., 3000 cm^3, 122 kW at 3500 rpm, maximum torque 380 Nm), where the temperature and gas composition before and after the trap can be controlled and monitored, as well as the evolution of the pressure drop through the trap, being a sign of soot accumulation therein (Fig. 1). The pressure drop across the trap could be measured by means of differential pressure transducers (VIKA) whereas the trap inlet and outlet temperature was measured by K-type thermocouples mounted at axial position. The soot concentration in the exhaust gases before and after the trap was measured by iso-kinetic sampling of a small flue-gas flow rate through a pump and by collecting the suspended particulate on a 2-filters system (PALLFLEX 47 TX 40 HI 20-W); the two measures are useful to determine the filtration efficiency. Finally, gas phase composition could be monitored through continuous analyser by Elsag-Bailey (NDIR for NO, CO, CO_2, SO_2; FID for overall HC; paramagnetic for O_2). The following standard bench test procedure was adopted: the trap was loaded by letting comparatively cold exhaust gases flow through it until a pressure drop of approximately 170 mbar was reached, corresponding approximately to a 10 g/l soot hold-up. Then, regeneration was induced by post-injecting some fuel (0.025 kg fuel/kg exhaust gases) with a metering pump (ISMATEC – Reglo CPF analog) and by burning it with an oxidizing honeycomb catalyst (OXICAT by Johnson Matthey) placed just upstream the trap so as to heat it up to about 550 °C. The time needed for the complete trap regeneration (e.g. combustion of soot hold-up) is an index of catalyst performance as well as the completeness of soot combustion. The higher the catalyst activity the lower the time required to regenerate the trap. The completeness of the regeneration process was indicated by the decrease of the trap pressure drop till a value practically equal to that measured at the beginning of the loading phase. A twin run on a virgin, non-catalytic trap was also performed for the sake of comparison.

Finally, the PM emissions were characterized in terms of particle size distribution, through exhaust gas sampling at the DPF outlet,

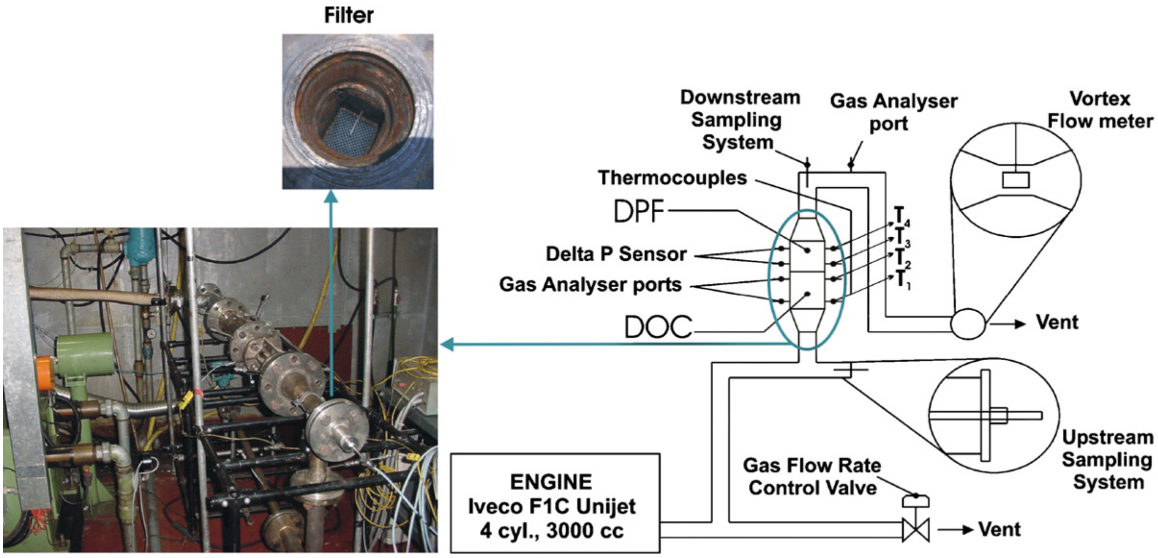

Fig. 1. Pilot plant for filter testing.

during both loading and regeneration phases, and were compared to the ones at the engine outlet and at the DOC outlet. The sampling system consists of two dilution stages (DEKATI DI-2000 package) connected to a TSI 3080 Scanning Mobility Particle Sizer (SMPS), each one ensuring an 8-fold dilution ratio. A first sampling pipe connects the sampling point to the first dilution stage, which is heated at 250 °C to avoid nucleation, while the second dilution stage is not heated and is directly connected to the SMPS. As a result, a total dilution ratio higher than 60 was achieved, which, according to the literature, should remarkably reduce particle agglomeration. At the end of the sampling system, a TSI 3080 SMPS [9] is composed of an electrostatic classifier TSI 3080 with a Kr-85 Bipolar Charger using Kripton as ion source, an inlet impactor 1035900, a differential mobility analyzer TSI 3081, and a condensation particle counter TSI 3025A.

3. Results and discussion

The characterization results regarding all the catalysts prepared are listed in Table 1. BET specific surface area (SSA) values ranging between 13 and 63 m^2/g were measured.

All delafossite samples were found to be well crystallized by XRD analysis (Fig. 2), whose spectra are reported here for the stoichiometric ($LiCrO_2$) and sub-stoichiometric at the B site ($LiCr_{0.9}O_2$, $LiCr_{0.8}O_2$, $LiCr_{0.7}O_2$) delafossites, which showed the best performances based on the results contained in Table 1. All diffraction peaks expected according to the reference JPCDS card ($LiCrO_2$, PDF 24-0600) were observed. No secondary phases could be detected by this technique (X-ray diffraction has a ±4% sensitivity).

Table 1
Catalyst characterization results: BET specific surface areas and catalytic activity (loose contact).

Catalyst	BET (m^2/g)	T_p loose (°C)	$T_{5\%}$ loose (°C)
Non-catalytic	–	654	–
$LiCrO_2$	24.1	416	335
$LiCr_{0.9}O_2$	23.1	384	287
$LiCr_{0.8}O_2$	13.3	397	321
$LiCr_{0.7}O_2$	21.0	390	324
$Li_{0.9}CrO_2$	50.2	415	345
$Li_{0.8}CrO_2$	56.4	430	345
$Li_{0.7}CrO_2$	63.0	423	341
$LiCr_{0.9}O_2$ aged	5.5	497	385

FESEM pictures of $LiCr_{0.9}O_2$ delafossite catalyst produced via SCS show a spongy microstructure (Fig. 3). During solution combustion synthesis, the decomposition/combustion of reacting precursors generates a large amount of gaseous products in a very short period of time, which leads to a foamy catalyst morphology. By employing this direct observation technique, values of the catalyst grain size of 30–75 nm could be estimated (Fig. 3). The delafossite crystals sizes range well in agreement with the BET specific surface areas measured in case the mere geometrical surface area of the crystals is considered. Therefore, the SCS technique allowed obtaining extremely pure delafossites having a microstructure characterized by highly corrugated interfaces of the catalyst powder agglomerates; this turns into an intensification of the contact between catalyst and soot. In the present context, delafossite crystals having a size of the same order of magnitude of that of the diesel particulate aggregates (100 nm on average for the last generation of Common Rail Engines [10]) are expected to provide the highest specific number of contact points between these two counter parts.

The outcome of the TPC tests is depicted in Fig. 4-left: as expected, all of the catalysts significantly lowered the combustion peak temperature compared with that of the non-catalytic combustion. From both the onset temperature (5% soot combustion, determined form CO_2 plot integration) and CO_2 peak tempera-

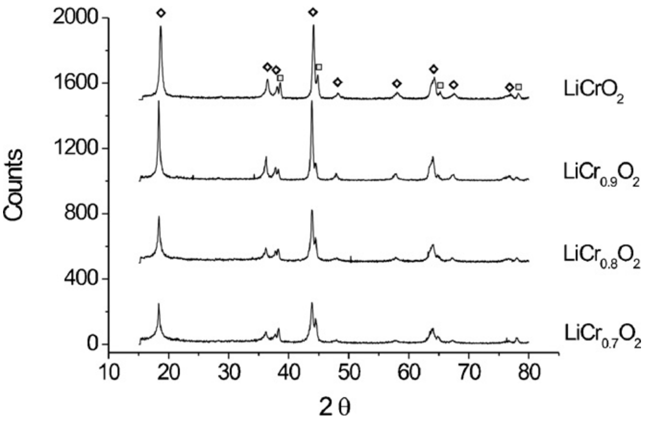

Fig. 2. XRD of delafossite powder catalysts: $LiCrO_2$, $LiCr_{0.9}O_2$, $LiCr_{0.8}O_2$ and $LiCr_{0.7}O_2$. Symbols: ◇ delafossite (JPCDS card PDF 24-0600); □ Aluminum sample holder (JPCDS card PDF 04-0787).

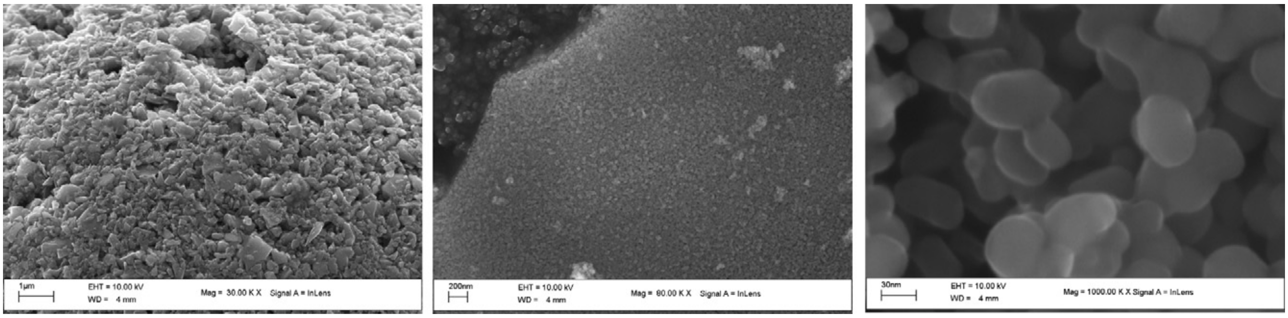

Fig. 3. SEM pictures of the powder $LiCr_{0.9}O_2$, at different degrees of magnification: 30k×, 80k× and 1000k×.

ture, listed in Table 1, an activity order can be outlined as follows: the $LiCr_{0.9}O_2$ showed the best activity by far under loose contact conditions (T_p = 384 °C); the other catalysts sub-stoichiometric at the B site exhibited quite similar activities (T_p = 390–397 °C); the unsubstituted $LiCrO_2$ and the other sub-stoichiometric at the A site delafossite catalysts exhibited quite similar activities (T_p = 415–430 °C) and were the least active catalysts. CO_2 selectivity (η_{CO_2}) for the catalyst-promoted soot combustion processes was always higher than 91% under loose contact conditions. The incomplete CO_2 selectivity recorded under loose contact conditions was possibly due to the influence, above about 450 °C, of direct non-catalytic oxidation pathways which are known to be less selective [5]. Transient thermal analysis studies were quite helpful for elucidating the soot combustion activity order of the prepared lithium chromites.

Fig. 4-right shows the results of hydrogen TPR runs regarding $LiCrO_2$ and the three B sub-stoichiometric delafossites. All the catalytic materials showed a reduction peak in the range 550–700 °C, following the order: $LiCr_{0.9}O_2 > LiCr_{0.8}O_2 > LiCr_{0.7}O_2 > LiCrO_2$. XRD data (not shown) of the catalysts after the reduction step showed that the delafossite structure was retained in all cases. Taking into account this last result, it is possible to deduce that, in order to maintain electro-neutrality, fresh catalysts containing chromium at a higher valence state get reduced during the TPR experiments to Cr^{3+}. By comparing the onset activity order of the synthesized catalysts with the TPR curves it can be inferred that the reduction of the B site is likely the key player in the catalytic combustion of carbon. The most active catalyst is the one which undergoes this reduction step with both the lowest onset temperature and the larger amount of reduced metal involved. From this viewpoint, it is not surprising at all that stoichiometric $LiCrO_2$ catalyst performed worse that the $LiCr_{0.9}O_2$ one, where the deficiency in Cr should have forced a corresponding fraction of Cr to increase its valence state from III to higher values [6] to preserve electro-neutrality. These high-valance Cr atoms should be responsible of catalyst reduction during TPR runs. It is more surprising that, when this Cr sub-stoichiometry was forced to higher values the catalyst activity was not further boosted but got even worse in performance, also if it remained better than the stoichiometric delafossite. Some possible reasons for this might be hypothesized:

- oxygen vacancies may be generated to compensate the severe absence of Cr atoms;
- small amounts of Li_2O, not detectable by XRD, might be formed.

XPS investigations were helpful to confirm these explanations. The amount of Cr with a higher valence state increased for the $LiCr_{0.9}O_2$ catalyst compared to the stoichiometric $LiCrO_2$ but remained unchanged for the delafossite catalysts having higher substitution values. As a consequence, it can be inferred that when a 10% chromium substoichiometry is imposed, electroneutrality should actually be enabled by a simple shift in chromium valence, very effective in terms of enhancement in catalytic activity. Higher Cr sub-stoichiometries simply did not turn into a further increase of the amount of high-valence chromium detected, which may cause appearance of either oxygen vacancies or formation of small amount of Li_2O, detrimental for the catalytic activity. In particular, Fig. 5 compares XPS spectra in the O 1s region of the stoichiometric ant the best delafossite catalysts. It is generally accepted that the O 1s peaks can be deconvoluted into oxygen lattice (O^{2-}) at a lower binding energy and surface adsorbed oxygen (O^-) at a higher bonding energy. By deconvoluting the O 1s peaks in the high-resolution XPS spectra of $LiCrO_2$ and $LiCr_{0.9}O_2$ to the peak at about 530 and 532 eV, we found that the ratio of the peak assigned to the surface adsorbed oxygen (531.5–531.9 eV) is 1.82 times larger in $LiCr_{0.9}O_2$ than that in $LiCrO_2$. This implies that the before mentioned Chromium redox behavior is connected with the delafossite catalytic activity through the capability to pro-

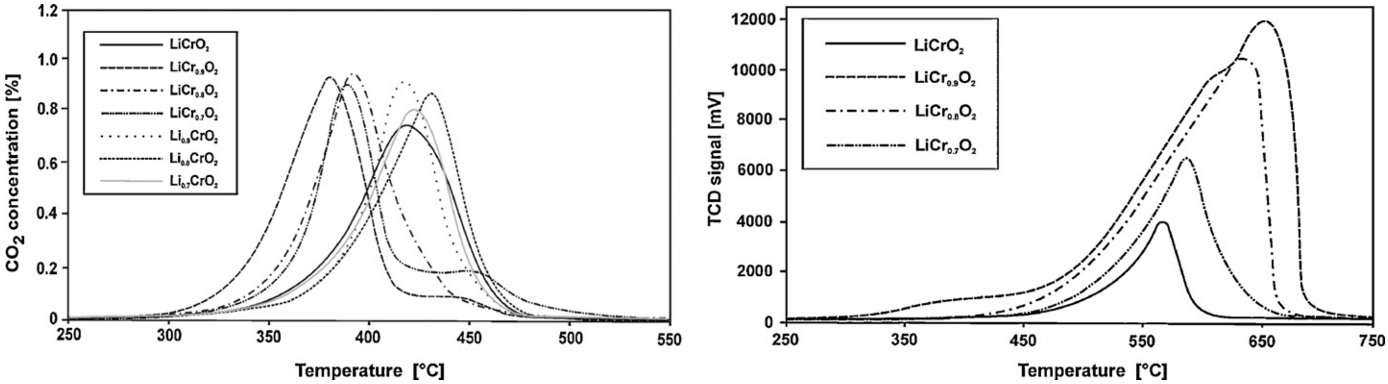

Fig. 4. Left: temperature-programmed combustion (TPC) runs performed with all the prepared delafossite catalysts. Right: hydrogen temperature-programmed reduction (TPR) tests on some selected delafossite catalysts.

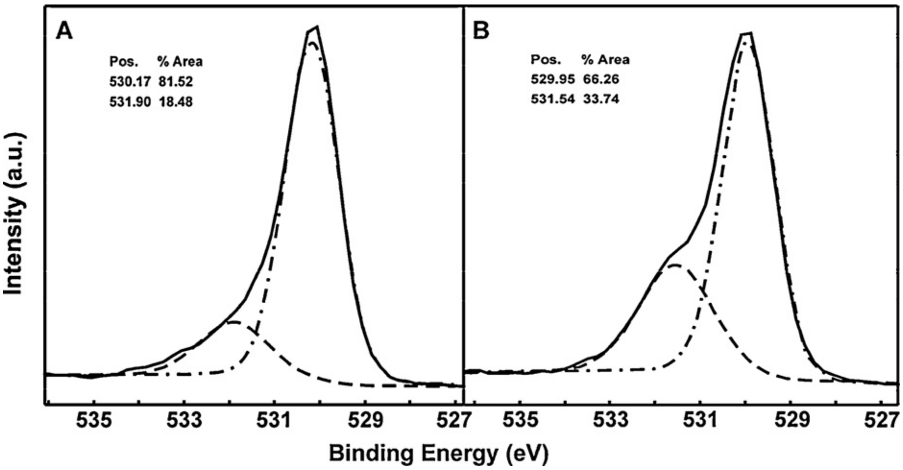

Fig. 5. X-ray photoelectron spectra in the O 1s region of: (A) $LiCrO_2$; (B) $LiCr_{0.9}O_2$. Dashed line: O^- species; dashed-dotted line: O^{2-} species.

vide the higher amount of weakly chemisorbed surface oxygen [6].

The outcome of the aging test on the $LiCr_{0.9}O_2$ catalyst, carried out by exposing the fresh powder to an atmosphere containing $10\%_{vol}$ of steam and 500 ppm of SO_2 in air, for 6 h at 800 °C, resulted in a certain loss of activity: from the last row of Table 1, it can be seen that the specific surface area decreased to $5.5\,m^2/g$ and the on-set temperature increased by 97 °C, as approximately did the peak temperature: the latter is anyway more than 150 °C below the values for the non-catalytic combustion. One has to highlight that the aging protocol was characterized by very severe operating conditions, and could be taken as representative of even high temperature soot combustion, occurring in transient dynamics which are peculiar of the ever-changing driving conditions. In addition, the SO_2 concentration is very conservative if compared to the current concentration in the exhaust flue gases from diesel engines, and could be considered indeed representative of a long-lasting performance.

Since the highly sub-stoichiometric catalysts were less effective than the $LiCr_{0.9}O_2$ one, only this last catalytic material was further investigated in combination with a diesel particulate trap. Fig. 6-left A shows a FESEM micrograph of the NGK wall-flow monolith deposited by *in situ* SCS with the $LiCr_{0.9}O_2$ catalyst. In particular, a FESEM micrograph of a single channel is shown in Fig. 6-left B, from which the highly porous catalyst layer having a thickness ranging between 20 and 40 μm can be seen. During combustion synthesis, the decomposition of reacting precursors generated a large amount of gaseous products in a very short period of time, which led to a spongy catalyst morphology. As mentioned earlier, this feature represents a great advantage, as it favors the contact between the catalyst and the soot and keeps at acceptable values the pressure drop increase (≅5%) due to the presence of the catalyst itself. On the grounds of standardized vibration tests, the adhesion of the deposited catalytic layer was found to be quite good (catalyst loss < 0.8 wt% after severe tests assumed as representative of an entire operating lifetime of a trap [11]).

Shifting to the analysis of the developed trap systems performance, Fig. 6-right compares the results of the runs obtained with the catalytic and the reference, non-catalytic NGK SiC wall-flow monolith. The results are rather encouraging. After loading up

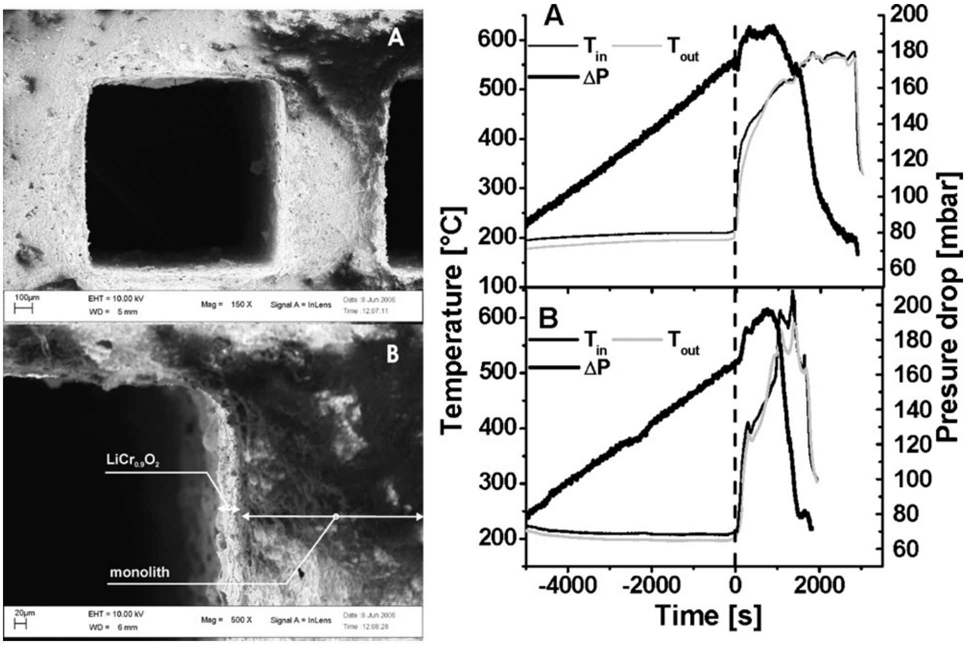

Fig. 6. Left: FESEM micrographs at two different magnification levels of a $LiCr_{0.9}O_2$-catalyzed trap based on an NGK SiC wall-flow monolith prepared by *in situ* SCS: (A) 150×; (B) 500×. Right: results of loading and regeneration runs for (A) virgin and (B) $LiCr_{0.9}O_2$-catalyzed traps.

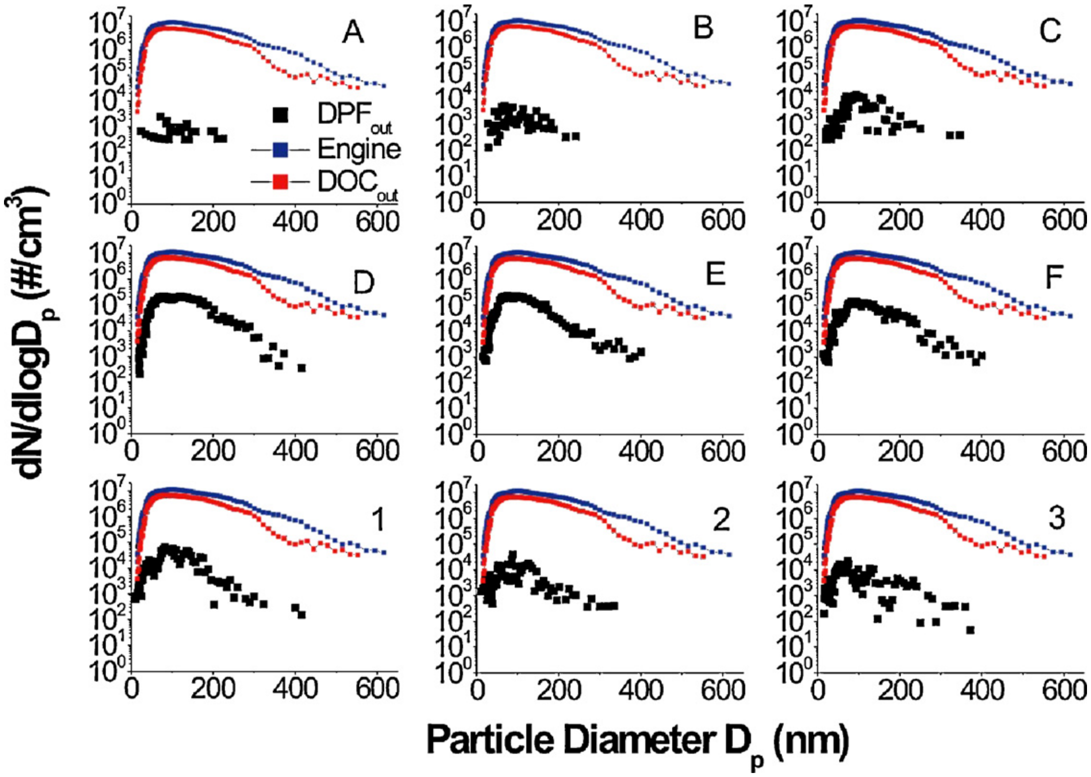

Fig. 7. PM emission during $LiCr_{0.9}O_2$-catalyzed trap regeneration. A: $t = 0$ (regeneration start); B: $t = 5$ min; C: $t = 10$ min; D: $t = 18$ min; E: $t = 22$ min; F: $t = 29$ min (regeneration end); 1: $t = 17$ min; 2: $t = 19$ min; 3: $t = 27$ min.

the trap till a pressure drop of ≅170 mbar was reached, the post-injection of fuel was operated. This entailed a rapid increase in the inlet trap temperatures as measured by a thermocouple inserted some 10 mm inside one of the central channels of the trap. However, upon reaching a temperature level just exceeding 450 °C, the regeneration of the catalytic trap gets started (Fig. 6-right B), as shown by this occurrence. The regeneration of the $LiCr_{0.9}O_2$-catalyzed trap was much faster than that of the non-catalytic ceramic filter, which resulted in a nearly one-third fold shorter soot combustion period (evaluated from the starting point of the post-injection). Similarly, the $LiCr_{0.9}O_2$-catalyzed trap exhibits a better performance than a reference commercial catalytic trap, based on an Ibiden SiC monolith and coated with an Engelhard Pt catalyst, already tested within our group [12]: in fact, the latter required roughly 1250 s to reduce the pressure drop by 45 mbar, starting from the same initial soot loading (10 g/l) and at the same regeneration temperature (600 °C), while the $LiCr_{0.9}O_2$-catalyzed trap reduced the pressure drop by 90 mbar in about 1500 s.

By significantly lowering the soot combustion temperature, it becomes possible to save a significant amount of fuel at any filter regeneration, thereby reducing the operating costs. It should be remarked, however, that part of the fuel saving cost is compensated by a very small decrease of filter permeability due to the presence of the catalyst, which brings about the above mentioned small additional back pressure. Another important feature lies in the much more complete regeneration of the catalytically promoted trap, which is proven by the fact that, despite the higher intrinsic pressure drop (≅5%), the final pressure value after regeneration was ≅10 mbar lower than that of the non-catalytic trap. This is a sign of a lower residual soot hold-up. By proper weight measurements, performed after regeneration, it could be noticed that 78% of the trapped soot was actually burned out for the catalytic trap, whereas this percentage was significantly lower (53%) for the non-catalytic counter part. As a consequence of this more complete regeneration, a lower regeneration frequency can be expected for the catalytic trap, compared to the non-catalytic one, which should result in further savings in post-injected fuel.

Finally, an experimental campaign was carried to assess PM emissions, in terms of particle size distribution, during the regeneration of the $LiCr_{0.9}O_2$-catalyzed trap: Fig. 7 shows how cake combustion reduces the filter ability to retain soot particles until a minimum filtration efficiency is reached at regeneration completion (emissions from A to F). In particular, A is the regeneration start condition, at which the trap exhibits the maximum particle filtration due to the soot cake collection mechanism. This efficiency can be observed by comparing the difference between the PM emissions at the DOC outlet (i.e. DPF inlet) and at the DPF outlet, while the DOC effect is negligible since no relevant abatement occurs as compared to the outlet engine emissions. As soon as regeneration proceeds, the soot layer is progressively consumed, whose effect is a PM emission increase (B–F) of two orders of magnitude, due to an increased trap permeability. Finally, at regeneration completion, a new soot cake is built up in the filter channels (1–3), and the DPF particle capture ability is progressively recovered.

4. Conclusion

Several Li–Cr delafossite catalysts ($LiCrO_2$, $LiCr_{0.9}O_2$, $LiCr_{0.8}O_2$, $LiCr_{0.7}O_2$, $Li_{0.9}CrO_2$, $Li_{0.8}CrO_2$ and $Li_{0.7}CrO_2$) were prepared by the SCS method, characterized, and tested as catalysts for diesel soot combustion under loose contact conditions. The $LiCr_{0.9}O_2$ catalyst exhibits the highest activity ($T_p = 384$ °C) as a consequence of its greater easiness to be reduced, to provide surface weakly adsorbed oxygen to the combustion reaction, at the lowest on set temperature. These oxygen species can be likely pointed out as the key players in the soot oxidation process. Moreover, the present investigation proved that a wall-flow ceramic filter catalyzed with $LiCr_{0.9}O_2$ obtained by *in situ* SCS looks very promising for diesel soot removal for light duty vehicles. It entailed for the trap structure tested a one-third fold reduction of the time required for trap regeneration (and of the related fuel penalty) as well as a much more complete regeneration compared to that of a non-catalytic trap.

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