Catalytic Self Cleaning Surfaces for Household Oven

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1. Introduction

The present work is aimed at investigating an improved automated cleaning process, capable of satisfying both customer and manufacturers needs, significantly reducing manual operations, by providing a cheaper alternative to pyrolytic ovens [1,2] with a similar added value. This aim will be pursued by developing oven walls with self cleaning properties, via catalytically enhanced thermal oxidation of soil at temperatures within the available range of standard ovens so to eliminate soil in real time during the cooking process. Oven soiling in mainly constituted by fatty acids splatters, thermally degraded by the prolonged exposure to oven walls temperature (up to 300°C), strongly adhered to the walls themselves. An automated cleaning product is implemented via high temperature (>500°C) cycles, lasting from 1 to 3 hours, organic remains are incinerated, hence easily removed as dust [3.4]. Several advantages could be reached by this system in terms of energy saving and economic materials to build the oven walls.

2. Experimental

Three different catalysts (CeO_2, $LaFeO_3$ and $MnCr_2O_4$) were prepared via a highly exothermic and self-sustaining reaction, the so-called "Solution Combustion Synthesis" (SCS) [5,6]. All the catalysts were then ground in a ball mill and characterized with: X-Ray Diffraction using a PW1710 Philips diffractometer equipped with a monochromator for the Cu-K_α radiation; BET specific surface areas by a Micromeritics ASAP 2010 analyzer.

Due to the extreme variability of composition of natural fats and of their partial degradation after the cooking process, three synthetic fatty acids (Myristic, Palmitic and Stearic), normally present in natural fats [7-9], were selected as a benchmark for the purposes of the present work.

The catalytic activity of the prepared catalysts was tested in a Temperature Programmed Combustion apparatus (TPC) described in [11]. TPC runs were subsequently performed for each catalyst/fatty acid combination, using the same procedure followed on the reference runs on bare acids. A TPC sample was prepared as a 1:9 w/w mixture of fatty acid and powdered catalyst, mixed in an agate mortar. This preparation leads to contact conditions between catalyst and reagent that can be described as "tight"; such situation is indeed quite intensive, if compared to what is actually achievable on an oven muffle surface, but enables a much higher degree of reproducibility, which is essential for activity screening studies.

The carbonaceous substance conversion was monitored via a NDIR analyser (Hartman and Braun URAS 10E) by measuring the carbon dioxide and monoxide concentrations in the reactor exhaust gases. The CO/CO_2 outlet concentrations increased starting from the carbonaceous substance ignition temperature, reached a maximum, and then decreased as a consequence of carbon consumption. For catalyst activity experiments, the temperature corresponding to the CO_2 peak (T_P) was taken as an index of the activity of the tested catalyst, while the CO release was qualitatively considered as an indicator of catalyst selectivity. The

runs were in all case repeated three times and the average T_P value was assumed for each catalyst.

In order to fully appreciate the catalyst performance, blank TPC experiments, using air as flowing gas, in the presence of the sole inert SiO_2 particles (0.1 mm in size) were carried out for each fatty acid. After such experiments, T_{P0} and T^*_{P0}, defined respectively as CO_2 and CO maximum release peak temperature of the bare carbonaceous substance, could be identified.

A quantitative measurement of the catalyst effectiveness was the decrease of activation energies for fatty acids combustion reaction: the Ozawa's method proved to be well suitable for calculating activation energy starting from experimental results obtained by Differential Thermal Analysis (DTA). Differential thermal analysis runs were performed by using a Perkin-Elmer equipment in the temperature range from 50 to 720°C with different heating rates (2, 5, 10, 15 °C/min) and under an air flow of 100 Nml/min. In this case, palmitic acid was used as reference substance for fatty acids.

The Spray Pyrolysis Process (SPP) is particularly suitable to *in situ* synthesize inorganic compounds over a flat, even surface, as the oven muffle internal one [14]. Enamelled steel samples (Ferro Perc™ Enamel, from a stock drip pan) to be coated by the catalysts were heated up to 500°C (similarly to the SCS experiments previously described). A subsequent heat treatment at 600°C for 1h completed the combustion process and allowed the full development of the catalyst crystalline structure. Even if the precursor chemistry and light-off temperature of the SPP process used were identical to those of the SCS technique, a significantly different microstructure of the catalyst was expected, due to different synthesis conditions and dynamics. In particular, being the spray process potentially uneven, the uniformity of catalyst layers was investigated by observing, over several prepared samples, different small areas.

Scanning Electron Microscope (Philips, Model 515) was used to analyze the microstructure of the deposited catalyst layers, and their elemental composition was checked by EDS analyses. The activity of catalytic coated plates by SPP was evaluated and benchmarked using a food derived fat substance, namely pork lard. A solid substance was selected so to avoid dripping during the experiment setup, possibly jeopardising the final results.

Gravimetric measurement of catalyst activity was evaluated on the basis of a reference sample baseline, in a comparative way. Reference sample reported after cleaning cycle a certain amount of weight loss, that can be related to fatty substances evaporation and partial degradation mechanisms not associated to catalyst activity. Such amount of weight loss was subtracted to the starting soil mass, so as to obtain the soil mass remaining after the cleaning cycle in absence of catalysis. The activity of catalytic coatings was hence evaluated as the percentage value of the residual soil as previously defined, detected by gravimetric measurement of the samples after each cleaning cycle.

3. Results and Discussion

Figure 1 shows the non catalytic TPC run of the stearic acid as an example of the double step combustion process. The other two fatty acids showed a very similar combustion trend. The weight loss of 80% occurred at 300-380°C, a temperature range in which the developed catalysts could indeed work as oxygen pump and promote catalytic oxidation [11, 15-16]. The TPC plots were in good agreement with TGA data, and in particular, the multi-step combustion process was as evident as in TGA experiment. Noticeably, CO_2 emission occurred in all cases in a two-step mode: the CO_2 peaks were named T'_{P0} and T''_{P0}. CO emission peak T^*_{P0} was essentially connected with the first CO_2 peak T'_{P0}: this suggested that the first step of combustion had a much quicker kinetic, resulting in oxygen shortage and CO formation. All the three combustion processes were completed at temperatures between 500 and 620°C (Table I).

It can be argued that during the first combustion stage (see fig.1) the direct oxidation of the organic compounds was accompanied by formation of harder to oxidise intermediates which met complete oxidation in the second combustion stage. Actually, this second stage occurs at typical temperatures at which carbonaceous compounds usually burn out [11].
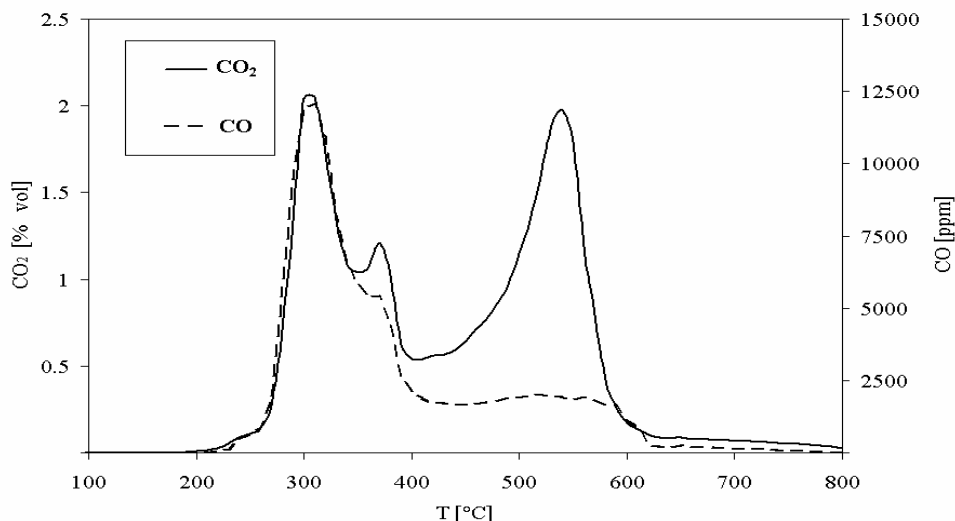

Figure 1. Stearic acid TPC run: CO/CO₂ emission curves

Table I. TPC runs of fatty acids: T'_{P0}, T''_{P0} and T^*_{P0} values summary

Fatty acid	CO₂ Peak Temp. T'_{P0} [°C]	CO₂ Peak Temp. T''_{P0} [°C]	CO Peak Temp. T^*_{P0} [°C]
Myristic	300	540	310
Palmitic	280	435	295
Stearic	310	540	310

Shifting to catalysts characterization, all prepared catalysts were found to be well crystallized by XRD analysis (not reported). All the main diffraction peaks listed in the reference JPCDS cards (LaFeO₃: PDF 75-0541; MnCr₂O₄: PDF 75-1614; CeO₂: PDF 65-2975) were observed. FESEM analysis results (not reported) enlightened for the three catalysts a very foamy structure, a typical feature of catalysts synthesized by SCS. The crystals size of the considered catalysts ranged between 60 and 100 nm, which is in substantial agreement with the specific surface areas measured.

The catalytic activity tests for the catalyst-acid mixtures carried out in the TPC apparatus gave interesting results. The CO₂ and CO emission profiles (see Figure 3 for those related to LaFeO₃ TPC experiments) show a severe change in the combustion reaction mode: the multi-step combustion process disappeared, resulting in a single step process. Considering the mean value of T'_{P0} and T''_{P0} (referred as T_{P0}) from Table II as a reference one for the whole two-step reaction experiment (420°C for Myristic Acid, 360°C for Palmitic Acid, 425°C for Stearic Acid) and the achieved T_P values of single-step catalyzed reaction (quite similar for all three acids), the difference $\Delta T_P = T_{P0} - T_P$ can be considered as a parameter quantifying the positive effect of the catalysts. The calculated peak shift ΔT_P of each catalyst are reported in Table IV.
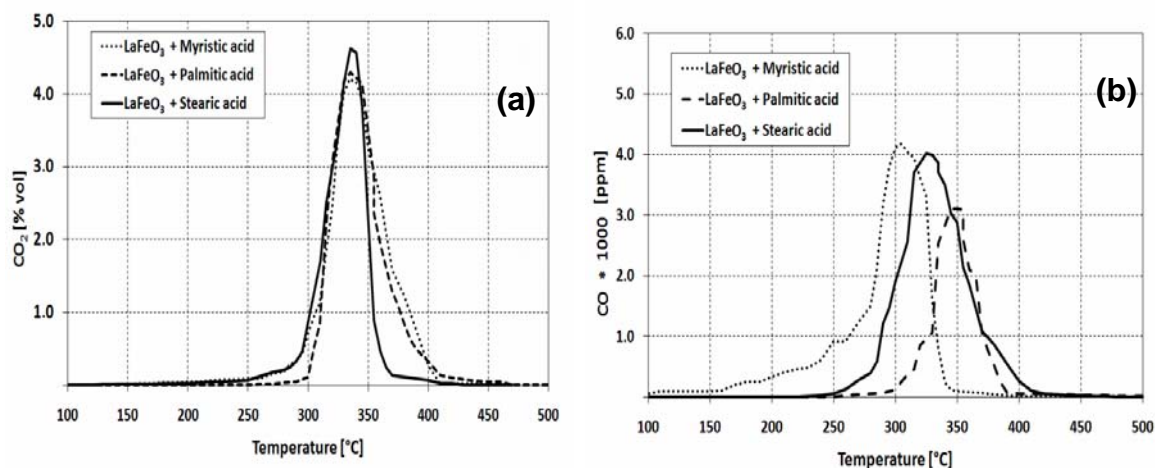
Figure 2. LaFeO$_3$ activity on selected fatty acids – TPC runs; (a) CO$_2$ emission graphics; (b) CO emission graphics

Table II. Catalyst activity evaluation: CO$_2$ on fatty acids: table of T_P and T^*_P

Fatty Acid	Uncatalysed reaction T_{P0} [°C]	CeO$_2$ related ΔT_p [°C]	LaFeO$_3$ related ΔT_p [°C]	MnCr$_2$O$_4$ related ΔT_p [°C]
Myristic	420	-100	-90	-50
Palmitic	360	-45	-25	30
Stearic	425	-105	-90	-35
		Average ΔT_p [°C]		
		-83	-68	-18

CeO$_2$ showed the best performance, followed by LaFeO$_3$ and MnCr$_2$O$_4$. The latter, however, exhibited the best selectivity towards CO$_2$ (about 92%).

The calculated activation energies for the bare and catalysed palmitic acid are reported in Table III. The obtained combustion activation energy reduction were perfectly in agreement with the TPC tests results. This is in line with the ideal behaviour of a heterogeneous catalytic process, where also the reactant is in the solid state: mass transport plays in this case a minor role, being driven exclusively by geometrical contact conditions, set on purpose as tight, as explained earlier. Also, the gaseous reactant (i.e. oxygen) was provided in large excess, fully permeating the fixed bed reactor.

Table III. Activation energy of Palmitic Acid combustion in air
in presence of the prepared catalysts, calculated by Ozawa's method

	Combustion activation energy [kJ/mol]
Palmitic Acid	88,58
Palmitic Acid + CeO$_2$	47,58
Palmitic Acid + LaFeO$_3$	51,74
Palmitic Acid + MnCr$_2$O$_4$	82,17

As concerns the complete enamel-catalyst-soil system, SEM images reported in Figure 3 show the CeO$_2$ coatings after the SPP deposition process.
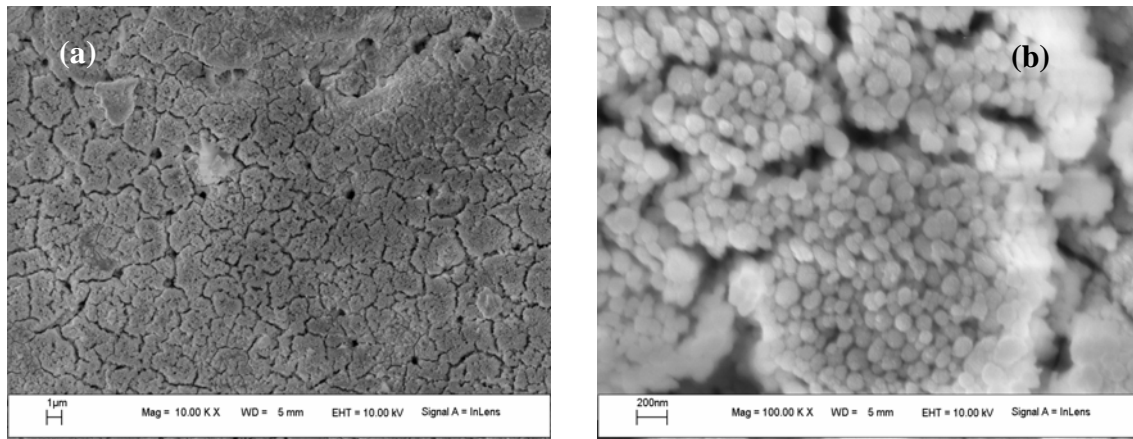
Figure 3: FESEM views of SPP CeO$_2$ layer lined on enameled steel; (a) 10Kx; (b) 100Kx

A general characteristic of all three coatings was a certain degree of grazing; surface cracks appear generated from surface round holes, most probably deriving from evacuation of the gaseous species generated during precursors decomposition. In all three cases, a clearly developed foamy microstructure was present, under the form of grains having an approximate dimension from 50 to 200 nm. The catalysts activity of the coated enameled steel towards the combustion of pork lard are reported in Figure 6. The effect of catalytic coatings is evident, if compared with the non catalyzed plate. CO and CO$_2$ emission plots showed that, at the selected target temperature (300°C), the non catalyzed pork lard combustion was relatively slow and prolonged well beyond the set experiment time, moreover developing a noticeable amount of carbon monoxide. Catalyst assisted processes showed a significantly more favorable performance, resulting in a peak-shaped emission curve of both CO and CO$_2$, ending inside the imposed test time of 60 minutes (40 minutes for CO). The beneficial effect of the catalyst layer appeared then to be clearly marked, even under operative conditions far from those in the first set of TPC experiments performed on powders. It is also worth noticing that combustion light-on occurred, especially for CeO$_2$, at temperatures around 200°C.
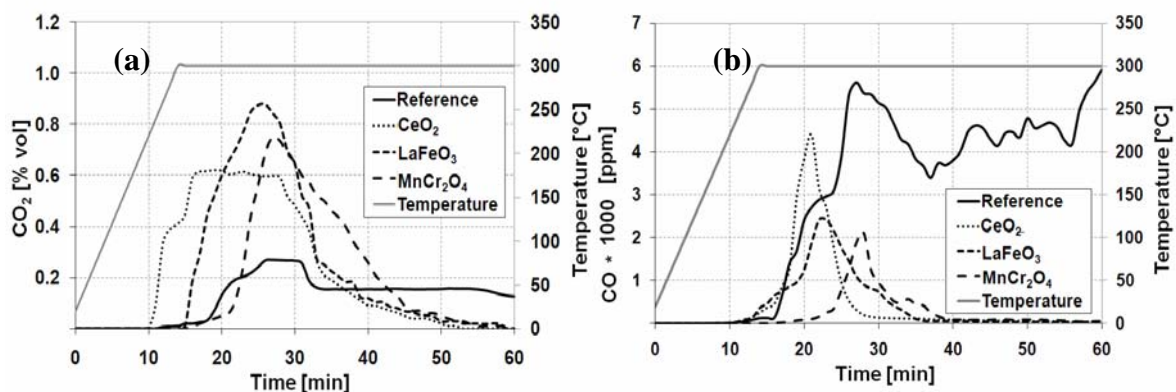

Figure 4: SPP catalyst activity on pork lard – TPC runs: CO$_2$ (a) and CO (b) emissions

Figure 5 shows the per-cent abatement of both pork lard and olive oil during the catalyzed combustion cycles in oven. A certain scattering of results was detected, as reported by the error bars, attributed to the unavoidable limitations in test reproducibility. The achieved results were of sure interest for the foreseen industrial application: the tested catalysts, activated via the above described thermal cleaning cycle, removed more than 15% in weight

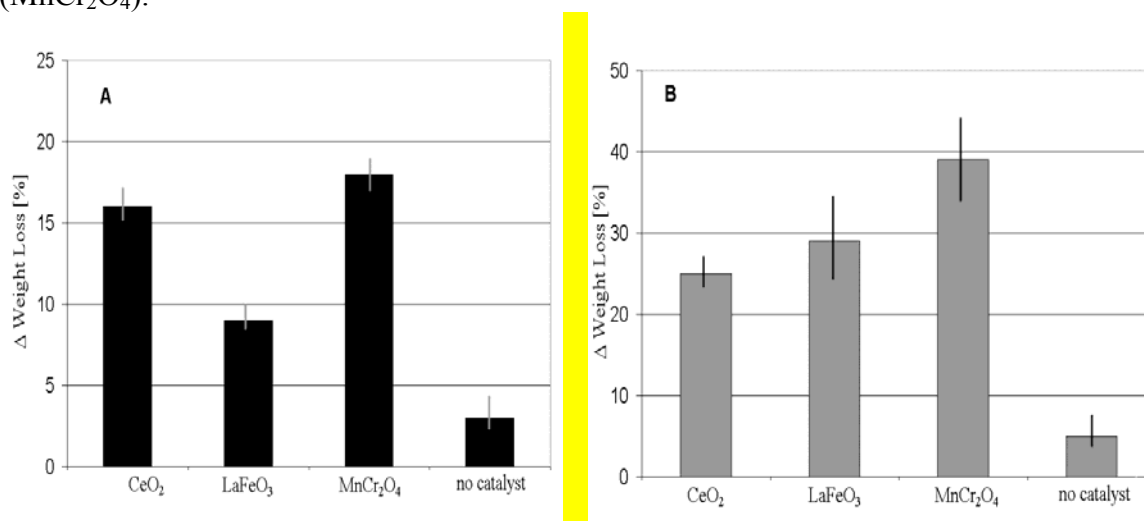of pork lard (CeO_2 and $MnCr_2O_4$), and up to 40% of the residual soil from olive oil ($MnCr_2O_4$).

Figure 5: SPP Catalyst activity towards (A) pork lard and (B) olive oil combustion in a stock oven: weight loss of soil (referred to bare enamel as reference) due to the catalysts effect.

On such a basis, it is possible to foresee a significant reduction of soil accumulation rate as a consequence of the catalytic combustion effect occurring during normal cooking cycles, even though, for maintaining the catalytic activity, a periodic cleaning cycle is probably required. This is obviously related to the specific cooking habits. For instance, if a soil generating cooking process is followed by several ones with a limited soil production, complete self-cleaning could be achieved. In any case, the regeneration cycle would be characterised by temperatures (about 300°C) much lower than those typical of the pyrolytic cycle (about 500°C).

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