Perovskite coatings in microwave - assisted soot filter regeneration
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Summary

Exhausts of vehicles have attracted increasing attention in last three decades. Some components emitted from vehicle engines, i.e. CO, HC, NO\textsubscript{x}, and soot, have been proved to be hazardous to human health. Although exhausts of gasoline engines, i.e. CO, HC and NO\textsubscript{x}, have been successfully cleaned up by three-way catalysts, such catalytic device is seen to be unreliable for reduction of soot emissions produced by Diesel engines, since a minimum exhaust temperature of approximately 673 K to 723 K is necessary to initiate and sustain soot burn-off. Due to too low exhaust temperature, it is required either to raise the off-gas temperature, or to heat the entire filter element to soot light-off temperatures. An alternative is the use of microwave energy - as dielectric heating is a bulk technique, it is faster than heating based on conduction.

The primary goal of the research presented in this thesis is to assess the feasibility of using a microwave sensitive, catalytic material as a filter coating. By periodically subjecting it to a dielectric field, the coating is allowed to reach soot ignition temperatures, resulting in self-sustained carbon burn-off. Perovskite-type oxides have been chosen as the coatings, since these oxides show a high catalytic activity and high resistance to deactivation by hydrothermal sintering, and have favourable dielectric properties. Moreover, as compared to noble metals, they are much cheaper. This thesis is focused on one type of perovskites, La\textsubscript{1-x}Ce\textsubscript{x}MnO\textsubscript{3}. They have been intensively investigated with respect to physical properties, catalytic properties and dielectric behaviour.

In Chapter 1, an overview is given with respect to the environmental impact of diesel soot, soot emission standards, and the currently known techniques for reduction of soot emitted from Diesel engines along with their limitations. The principle of the proposed microwave-assisted soot filter regeneration is explained in detail. A concise description of dielectric heating and existing dielectric susceptors, including perovskites, is given. The physical properties with respect to crystalline structure and non-stoichiometry, as well as catalytic properties in oxidation reactions, reduction of NO\textsubscript{x}, and SO\textsubscript{2} poisoning and regeneration aspects are discussed in detail. The dielectric properties of perovskites
related to the temperature, phase transition, tolerance factor, ionic size and substitution are briefly summarised.

Study of surface properties and catalytic performance is important for better understanding of perovskites as active catalysts. **Chapter 2** focuses on characterisation of La-Ce-Mn perovskites using XRD, XPS, TEM, TPR and TPO, and on catalytic activity of these perovskites in CO oxidation. A single perovskite crystalline structure is formed for a low degree of Ce substitution (x up to 0.1). Beyond $x = 0.2$, a separate CeO$_2$ phase is formed. Substitution of La by Ce results in enhanced catalytic activity in CO oxidation, the highest activity being exhibited by La$_{0.8}$Ce$_{0.2}$MnO$_3$. XPS data show that the Ce substitution is accompanied by an increasing concentration of cation/anion vacancies in the perovskite lattice, which leads to a shift in the Mn$^{4+}$/Mn$^{3+}$ ratio. The number of those vacancies is directly related to the catalytic performance by facilitating CO adsorption. However, the formation of a significant amount of catalytically inert CeO$_2$ leads to a drop in the catalytic activity for $x$ beyond 0.2.

The mechanism of CO oxidation over La$_{0.8}$Ce$_{0.2}$MnO$_3$ perovskite has been investigated using step-response analysis (transient). In this way, information can be obtained on the elementary steps of a reaction, since the time-resolved observations allow quantitative assessment of the accumulation of species on the surface. In **Chapter 3**, mechanistic details of CO oxidation over this perovskite are revealed by performing isothermal reduction and oxidation of the catalyst through switching the gas mixture from He to either CO or labelled and unlabelled O$_2$. Full reversibility of the oxygen uptake is observed at a temperature of 473 K and higher. It is concluded that oxygen from the perovskite lattice is involved in reduction and oxidation reactions. Stable species, most likely bidentate carbonates, are retained on the reduced oxide surface. Oxygen can adsorb dissociatively on a partially reduced surface, giving rise to a low activation energy. Two reaction mechanisms are involved in CO oxidation: ER (Eley-Rideal) and LH (Langmuir-Hinshelwood) mechanisms. Similar to reduction and oxidation, the formation of CO$_2$ by CO oxidation proceeds through an intermediate carbonate species that subsequently decomposes.

As an addition to the intensive study of the physical and catalytic aspects related to catalytic performance in oxidation reactions, the dielectric properties of these Ce substituted La-Mn based perovskites as microwave susceptors have been investigated and reported in **Chapter 4**. While some sintering occurs during dielectric heating in He, no
significant bulk changes are observed, indicating that these perovskites are highly thermally stable. Dielectric permittivities in the microwave and radio frequency regions for the pressed perovskite pellets are measured by the open-ended coaxial line dielectric probe method at room temperature, while the values for the solid materials have been calculated from generalized Looyenga equation. High values of dielectric permittivities are found at low frequencies, related to ionic conduction, while at microwave frequencies, storage and loss proceed through dipolar reorientation. A relatively low dielectric constant and low loss are found for $x = 0.05$, indicating a small contribution of ionic conduction, as the result of annihilation of ionic defects by Ce doping. An increase of the dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) is found with increasing amounts of Ce up to $x = 0.2$, as a result of the formation of a larger number of cation/oxygen vacancies. For $x = 0.3$, a decline in both dielectric constant and loss is observed, which can be ascribed to the formation of large amounts of CeO$_2$, which has low dielectric permittivity.

A study of the catalytic activity and resistance towards SO$_2$ poisoning over La$_{0.8}$Ce$_{0.2}$MnO$_3$ during dielectric heating, using CH$_4$ oxidation as model reaction, has been reported in chapter 5. As a comparison, the same reaction is carried out during conventional heating. High catalytic activity towards CH$_4$ oxidation over this perovskite is observed during dielectric heating, as compared to heating conventionally. This has been explained by the existence of local hot spots on the catalytic surface. Deactivation of this perovskite by SO$_2$ is comparatively slow at high temperatures as a consequence of the weak adsorption of SO$_2$. However, irreversible loss in activity occurs after prolonged exposure to SO$_2$, which is attributed to the formation of Lanthanum sulphate. Cerium sulphate is formed predominantly during conventional heating, which contributes to the deactivation by elimination of anion vacancies that are responsible for the catalytic activity. Deactivation is faster for the reaction carried out by heating conventionally, due to the concerted effort of sulphate formation and the resulting pore blockage, which limits the accessibility towards the reactants. As pore blockage occurs mainly at the exterior of the particles during conventional heating, the result is a fast shell progressive deactivation. On the contrary, sulphate formation mainly occurs in the particle interior in the case of dielectric heating through a growing core mechanism. This leads to less fast deactivation.

Since La$_{0.8}$Ce$_{0.2}$MnO$_3$ perovskites have been proved to possess suitable catalytic and dielectric properties, this catalyst has been used as a coating material to assess the feasibility of microwave-assisted soot filter regeneration. Chapter 6 is devoted to soot filter
regeneration using synthetic carbon deposited on both a filter coated with a La$_{0.8}$Ce$_{0.2}$MnO$_3$ perovskite, and an uncoated filter. An uncoated soot filter may be regenerated in a dielectric field, since soot itself is a microwave sensitive material. However, the carbon light-off temperature can only be maintained for a short period as, due to the oxidation of carbon, not sufficient dielectric material remains to hold the required temperature. Moreover, substantial amounts of undesired CO are formed. In this chapter, soot filter regeneration has been improved significantly by using a La$_{0.8}$Ce$_{0.2}$MnO$_3$ filter coating. The regeneration is complete, fast and demonstrates a high selectivity towards CO$_2$. Moreover, this coating exhibits excellent thermal stability. Analysis of convective heat losses for cold inlet gases indicates that the soot light-off temperature of 700 K can be achieved for (realistic) space velocities up to 50,000 hr$^{-1}$. However, cavity modification is necessary, since the non-homogeneous electromagnetic field distribution in the travelling wave microwave system results in a broad temperature distribution across the filter.

In order to demonstrate the advantage of the use of a perovskite coating as compared to a non-catalytic filter, carbon burn-off was carried out for a much bigger monolith (4 cm diameter by 4 cm high) with and without the perovskite coating (see the figure below). This experiment shows that a more uniform temperature distribution across the filter is obtained for the filter coated with a perovskite coating, while some places in the filter remain cool for an uncoated filter.
In conclusion, this thesis has provided very valuable knowledge on the physical properties, catalytic performance and reaction mechanism of perovskite-type oxides, in particular of Ce substituted La-Mn based perovskites. By determination of the dielectric permittivities of the perovskites and thus assessment of the strength of coupling with the electromagnetic field, a relation between the heating efficiency and the elemental composition and crystalline structure of the perovskites can be drawn. Study of carbon burn-off demonstrates the feasibility of microwave-assisted soot filter regeneration using perovskites as coatings. Important directions of further work on this topic have been pointed out: cavity modification in order to obtain temperature uniformity across the filter and a broad study for variation of the elemental composition of perovskites with the aim to obtain more thermostable, catalytically active and poison resistant catalysts. However, also the economic implications of the use of this technique should be taken into account. Nixdorf et al. (SAE paper, 2001, 69-75) have already shown that an average 15 W would be sufficient for filter regeneration for a 1.9-L Volkswagen engine at a given engine load condition. This clearly indicates that implementation of this technique is in principle also economically feasible.