Chapter 7
Conclusions

Material synthesis
A series of lanthanum and barium based perovskite catalysts are synthesized by a modified citrate route and co-precipitation method respectively. These perovskitic structures are prepared for the first time at the facilities of the high temperature and functional coatings division of DLR’s Institute of Materials Research. A modified citrate route is employed to the synthesis of the lanthanum based perovskites. Care must be taken when working with nitrates in the presence of cobalt and iron since explosive mixtures can be formed. An additional care must be taken for the synthesis of the barium based perovskites. The co-precipitation method employed to synthesize these barium perovskites implies the use of metallic barium pieces. To avoid any exothermic reaction(s) and minimize the risk of explosion the metallic barium must not be brought into contact with aqueous solutions or water.

A single La-based perovskite phase with orthorhombic structure is synthesized by applying the citrate route. The Lanthanum based perovskite LaFeCo$_{0.3}$-Pd is amorphous upon calcination in air at 500°C and begins to crystallize into the orthorhombic structure at 550°C. The crystallization process of the perovskite LaFeCo$_{0.3}$-Pd ends at approx. 700°C. No other oxide phase(s), i.e. palladium oxide, are found after calcination in air up to 700°C by the XRD analysis, suggesting the formation of a solid solution between palladium and the perovskite. At higher calcination temperatures tetragonal PdO particles begin to diffuse out of the perovskite lattice and to grow, indicating the meta-stability of the produced perovskitic solid solution (LaFeCo$_{0.3}$-Pd).

The crystal sizes of the Ba-based perovskites BaTiO$_3$ obtained applying the co-precipitation method are remarkably smaller than the crystal sizes of the La-based perovskites obtained via the citrate route. The small crystal sizes of the Ba-based perovskites leads to a crystallization path that begins already at 500°C. Fully crystallized Ba-based perovskites are obtained, whereas the La-based perovskites are amorphous after calcination in air at 500°C. The perovskite phase BaTiO$_3$ is composed of a pure tetragonal perovskite with traces of BaCO$_3$. No other oxides such as BaO, TiO$_2$ or other mixed oxides are observed upon calcination up to 900°C, pointing out the success of this synthesis route to prepare the single phase perovskite. Barium carbonate is completely removed from the catalyst upon calcination in air at 900°C/3h.

Self-healing of palladium in the La- and Ba-based perovskites
The Pd-substituted perovskites are known with their adaptive character which induces an ageing resistance of the catalyst material. The occurrence of this characteristic is investigated in this study. According to the SEM and XRD observations the Pd-substituted La-based perovskite LaFeCo$_{0.3}$-Pd-700°C displays the diffusion of palladium out of the crystal lattice upon reduction treatment. Upon re-oxidation this second phase disappears indicating that the palladium ions may reversibly diffuse inside of the perovskitic crystal lattice (the self-healing property). For comparison purposes, the Pd-impregnated perovskite powders are synthesized to yield the palladium supported perovskite Pd-LaFeCo$_{0.35}$. In
contrast to the Pd-substituted perovskite, the as synthesized Pd-supported catalyst displays a second phase at the grain boundaries and on the surface of the perovskite indicating the presence of palladium particles sizes up to 40 nm.

The XPS analysis of the as prepared Pd-substituted perovskite LaFeCo\(_{0.3}\)-Pd indicates that palladium ions are partially incorporated into the crystal structure in this perovskite. On the other hand, in the Pd-supported perovskite, palladium is mainly on the surface and at the grain boundaries, however a partial dissolution of palladium has been observed on the first lattice layers of the perovskite particles. Palladium is reduced to metallic Pd\(^{\circ}\) at the supported perovskite Pd-LaFeCo\(_{0.35}\) under a hydrogen containing atmosphere already at 200\(^{\circ}\)C confirming the presence of mostly PdO on the catalyst surface in the oxidized state. In contrast, the palladium species in the Pd-substituted perovskite LaFeCo\(_{0.3}\)-Pd survive even after reduction in hydrogen at 500\(^{\circ}\)C. Palladium is partially dissolved into the crystal lattice in the Pd-supported perovskite Pd-LaFeCo\(_{0.35}\) upon calcination treatments. Moreover, different concentrations of palladium are recorded at the surfaces of both perovskites. The relative palladium concentration at the perovskite surface in the catalyst LaFeCo\(_{0.3}\)-Pd is considerably lower than the palladium concentration in the catalyst Pd-LaFeCo\(_{0.35}\) as determined by XPS indicating that a higher concentration of palladium is present in the bulk of the former than in the latter. Despite the fact that less Pd is readily available on the perovskite surfaces, the catalytic activity of the Pd-substituted perovskite [LaFeCo\(_{0.3}\)-Pd] is not inferior to that of Pd-supported perovskite [Pd-LaFeCo\(_{0.35}\)]. On the contrary, the Pd-substituted perovskite catalyst displays higher NO-conversions than the Pd-supported perovskite towards \(\text{C}_3\text{H}_6\)-SCR of NO with 5 vol. \% O\(_2\).

In the Pd-supported perovskite Pd-BaTi the XPS line of Pd 3d\(_{5/2}\) at 337.8 eV suggests that palladium is partially dissolved in the first layers of the perovskite lattice upon calcination treatment. These palladium species disappear upon reduction already at 200\(^{\circ}\)C forming metallic palladium Pd\(^{\circ}\) (BE Pd 3d\(_{5/2}\) = 334.2 eV). The XPS analysis of the Pd-substituted catalyst BaTi-Pd suggests that palladium ions are not fully incorporated into the perovskite lattice but highly dispersed on the perovskite surface. The relative concentration of palladium at the surface of the Pd-substituted catalyst (BaTi-Pd) compared to that in the Pd-supported catalyst (Pd-BaTi), also indicates that most of palladium in the Pd-integrated perovskite (BaTi-Pd) is inside the bulk structure. Even though less Pd is available on the catalyst surface no detrimental effect on the \(\text{C}_3\text{H}_6\)-SCR of NO\(_x\) reaction is observed with the Pd-substituted perovskite. Pd in the lattice and on the surface of both Ba-based perovskites is reduced to its metallic state Pd\(^{\circ}\) after the reduction treatments.

**Catalytic activity of the lanthanum based perovskites**

The Co-content in the La-based perovskites has a significant influence on their catalytic properties. There is a solubility limit of cobalt in the perovskite by the substitution at the B-site at the expenses of Fe. Cobalt oxide (Co\(_3\)O\(_4\)) has been detected in compositions with the Co- substitutions above 0.3 mol % in the B-site of the La-based perovskite. The decrease in Co-content from 0.475 to 0.3 fraction mol in the perovskite resulted in 14 % less NO\(_x\)-conversion at about 200\(^{\circ}\)C. Although, the catalyst powders contains only a single perovskite phase as the Co-content decreased down to the 0.3 mol, as mentioned above, the catalytic
activity towards the NO\textsubscript{x}-reduction suffer slightly. This indicates that the perovskite composition actively participates in the NO\textsubscript{x}-conversion process. The phase(s) composition of the La-based perovskite changes drastically with modification of the Co-content. The perovskite with Co-content of 0.475 mol % LaFeCo\textsubscript{(0.475)}-Pd is composed of the mixed orthorhombic and cubic perovskites. The split of the main XRD reflections, only observed upon heating, indicates the occurrence of both perovskites. This condition (i.e. Co\textsubscript{3}O\textsubscript{4} + the orthorhombic and cubic perovskites) in the catalyst holds in the presence of water vapour and CO\textsubscript{2} in the feed resulting in a better NO\textsubscript{x}-reduction and higher N\textsubscript{2}-selectivity of the catalyst LaFeCo\textsubscript{(0.475)}-Pd compared to the perovskite with lower Co-content. Although at temperatures above 240°C the presence of water vapour and CO\textsubscript{2} has as matter of fact a detrimental influence on the NO\textsubscript{x}-conversion capability of the low Co-content La-based perovskite catalyst (LaFeCo\textsubscript{(0.3)}-Pd) below 240°C. No measurable influence of the H\textsubscript{2}O + CO\textsubscript{2} addition on the NO\textsubscript{x}-conversion is detected. Positive effects of water vapour on the conversion of NO could be attributed to the presence of unknown metallic (or maybe bimetallic) species which dissociate the water molecules resulting in an increase of the coverage of chemisorbed hydrogen atoms. The hydrogen coverage may promote the dissociation of NO which is considered the rate determining step in the reaction. Identification and characterisation (i.e. conversion, selectivity, and adsorption-desorption properties measurements determination, etc) of the mentioned metallic species may provide answers to these questions.

Addition of CO in the feed (NO/H\textsubscript{2}) results in a decrease in the catalytic NO\textsubscript{x}-reduction and N\textsubscript{2}-selectivity of both Co-containing LaFeCo\textsubscript{(0.475)}-Pd and LaFeCo\textsubscript{(0.3)}-Pd La-based perovskite catalysts. Higher Co-content in the perovskite yields a better resistance against CO. The improved catalytic activity of the Pd-substituted perovskite with 0.475 mol % Co-content can be associated to some degree with the segregated Co\textsubscript{3}O\textsubscript{4}. A positive effect on the NO\textsubscript{x}-conversion due to phase cooperation may also be argued, however systematic studies are needed to elucidate this assumption. The LaFeCo\textsubscript{(0.475)}-Pd catalyst reduces 8 to 13 % more NO\textsubscript{x} and produces 10 to 50 % more N\textsubscript{2} compared to the performance of the perovskite with the lower cobalt content LaFeCo\textsubscript{(0.3)}-Pd.

The cerium solubility in the A-site of the La-based perovskite is very limited to less than 0.05 mol % Ce. In the present study a single phase is obtained in the perovskites La\textsubscript{(1-x)}Ce\textsubscript{x}Fe-Pd (x = 0.05, 0.1 and 0.4), after calcination in air up to 700°C. However, calcination of these perovskite compositions at 900°C showed that these phases are meta-stable and some traces of CeO\textsubscript{2} and Fe\textsubscript{2}O\textsubscript{3} segregate leaving back a LaFe-rich perovskite. A higher Ce-concentration (up to 0.4 mol %) [e. g. LaCe\textsubscript{(0.4)}Fe-Pd] delays the crystallization of the perovskite. As a matter of fact, the catalyst is amorphous displaying a disordered crystallographic characteristic. The crystallization of the catalyst occurs at 900°C by yielding rhombohedral Fe\textsubscript{2}O\textsubscript{3}, cubic CeO\textsubscript{2} and an orthorhombic perovskite. This catalyst displays a higher BET-surface area (6.647 m\textsuperscript{2}/g) compared to the La-based perovskite with the lowest Ce-content [LaCe\textsubscript{(0.05)}Fe-Pd] (1.598 m\textsuperscript{2}/g) on calcination at 900°C. The reason for this behaviour is the earlier crystallization temperature of low Ce-containing La-based perovskite which goes into a grain growth on calcination at 900°C. The best NO\textsubscript{x}-reduction performance and N\textsubscript{2}-selectivity for H\textsubscript{2}-SCR of NO\textsubscript{x} reactions may be relying on the relative high surface area of the catalyst LaCe\textsubscript{(0.4)}Fe-Pd. The catalyst LaCe\textsubscript{(0.4)}Fe-Pd displays high contents of Fe-
and Ce-oxides which strongly suggest the participation of these oxides in the improved NO$_x$-reduction performance of the catalyst. It would be mere speculation to say that these oxides may eliminate N$_2$O under the selected reaction conditions. The N$_2$O-decomposition determination of the single and mixed oxides of Fe- and Ce- under lean conditions could give insights in this direction.

Both the Pd-supported and Pd-substituted La-based perovskites yield similar NO$_x$-conversion performances under C$_3$H$_6$-SCR conditions and 1 vol. % O$_2$ in the feed. A maximum NO$_x$-conversion of 35 % is measured over these two perovskites at 250°C. Although the catalyst Pd-LaFeCo$_{(0.35)}$ displayed 20 % more NO-conversion than the palladium integrated catalyst LaFeCo$_{(0.3)}$-Pd with 1 vol. % O$_2$ at 225°C. An improved NO$_x$-reduction capability at higher oxygen concentrations (2 and 5 vol. % O$_2$) is observed over the Pd-substituted perovskite LaFeCo$_{(0.3)}$-Pd than over the Pd-supported catalyst Pd-LaFeCo$_{(0.35)}$. A maximum NO$_x$-conversion of 28 % of NO$_x$-conversion is detected at 225°C with 2 vol. % O$_2$ in the feed over the catalyst LaFeCo$_{(0.3)}$-Pd, yielding 2 to 7 % more NO$_x$ over the whole temperature range between 175° and 300°C than the supported catalyst Pd-LaFeCo$_{(0.35)}$. The catalyst Pd-LaFeCo$_{(0.35)}$ reduced 5 % more NO$_x$ than the palladium substituted perovskite LaFeCo$_{(0.3)}$-Pd with 2 vol. % O$_2$ in the feed only at 200°C. No explanation can be given to date for this result. Systematic and more experiments under similar reaction conditions are needed to convincingly validate these observations. With 5 vol. % oxygen in the gas mixture the maximum NO$_x$-conversion of 26 % is registered over the catalyst LaFeCo$_{(0.3)}$-Pd at 300°C, this perovskite reduces 2 to 10 % more NO$_x$ over the whole temperature range between 175°C and 300°C than the supported catalyst Pd-LaFeCo$_{(0.35)}$ with 5 vol. % O$_2$, the highest oxygen concentration tested in this study.

**Catalytic activity of the barium based perovskites**

The Pd-substituted Ba-based perovskite displayed 45 to 50 % of NO$_x$-conversions between 200° and 250°C under simple gas mixture (e. g. simple gas mixture includes NO, O$_2$ and H$_2$ with He as balance). A maximum NO$_x$-conversion of 73.2 % and N$_2$-selectivity of 82 % is measured over the Pd-substituted catalyst BaTi-Pd during the wet NO$_x$-reduction at 171°C. The presence of H$_2$O + CO$_2$ causes a positive effect on the NO$_x$-conversion and on the selectivity to nitrogen over this catalyst between 200°C and 270°C. At least in the presence of water the N$_2$O molecules are formed and not participate in any other reactions over the Ba-based catalyst. Positive effects on the NO$_x$-conversion over the Ba-based catalyst are probably related to the NO dissociation enhancement caused by water molecules. These assumptions need to be clarified in further studies.

The presence of CO in the reaction mixture causes a strong decrease in the NO$_x$-reduction and selectivity to nitrogen of this catalyst below 200°C, suggesting selective chemisorption of CO on probably the same catalytic active sites. The N$_2$O-formation obtained in the presence of CO is similar to the reaction in the presence of water + CO$_2$ (approx. 60 ppm), indicating that CO does not participate in the N$_2$O-formation over this catalyst. At a higher temperature the NO$_x$-conversion is negatively affected with CO in the feed and in comparison with some of the La-perovskites, less N$_2$O is produced which lead to a better
selectivity to nitrogen with the Ba-based perovskite. This catalyst reduced 10 to 20 % more NO\textsubscript{x} in the absence of CO in the temperature range between 150°C and 350°C.

In general the perovskite BaTi-Pd is one of the best catalysts in terms of NO\textsubscript{x}-reduction and N\textsubscript{2}-selectivity under the selected reaction conditions for H\textsubscript{2}-SCR of NO\textsubscript{x} reactions. Under simple reaction conditions (NO/O\textsubscript{2}/H\textsubscript{2}/He) the catalyst BaTi-Pd displays similar NO\textsubscript{x}-reduction levels (80 %) compared to the NO\textsubscript{x}-performance over the perovskite LaFeCo\textsubscript{0.3}-Pd. On these reaction conditions the Pd-substituted perovskite BaTi-Pd produces 22 % more nitrogen (or less N\textsubscript{2}O) than the Pd-substituted La-based catalyst [LaFeCo\textsubscript{0.3}-Pd]. The BaTi-Pd catalyst heat treated at 500°C/3h shows 25 to 30 % higher NO\textsubscript{x}-conversion at catalytic bed temperatures between 175° and 220°C than the same catalyst composition treated at 900°C/3h.

The Barium group of perovskites displays also the maximum NO\textsubscript{x}-conversion during the C\textsubscript{3}H\textsubscript{6}-SCR of NO\textsubscript{x} reaction between 200°C and 225°C with 1-5 vol. % O\textsubscript{2}. The propene light-off temperatures correspond well with the maximum NO\textsubscript{x}-conversion values obtained with the perovskites. The Pd-substituted Ba-based perovskite BaTi-Pd displays the highest NO\textsubscript{x}-conversion (42.4 %), with 1 vol. % O\textsubscript{2} in the feed, of all the tested perovskites in this work. Increase of the oxygen concentration to 2 and 5 vol. % increases the oxidation potential of the catalyst, which causes indeed the oxidation of propene at lower temperatures followed by a decrease in the NO\textsubscript{x}-conversion. The Pd-substituted perovskite BaTi-Pd displays a better NO\textsubscript{x}-conversion than the perovskite Pd-BaTi with 1 and 5 vol. % O\textsubscript{2} in the feed. The catalyst BaTi-Pd reduces 4 to 9 % more NO\textsubscript{x} than the perovskite Pd-BaTi during the reaction with 1 vol. % O\textsubscript{2} in the gas mixture. With 5 vol. % O\textsubscript{2} in the feed the catalyst BaTi-Pd reduces 4 to 5 % more NO\textsubscript{x} between 150°C and 200°C than the Pd-supported perovskite Pd-BaTi. At 225°C and higher temperatures the NO\textsubscript{x}-conversions are almost the same for both catalysts with 5 vol. % O\textsubscript{2} in the feed. The NO\textsubscript{x}-conversions obtained over these perovskites are similar with 2 vol. % O\textsubscript{2} in the gas mixture. These observations are unexpected because it implies that both catalysts pose the same NO\textsubscript{x}-conversion potential. On the other hand, the Pd-substituted catalyst BaTi-Pd displays a slightly better NO-conversion at 200°C and lower reaction temperatures than the Pd-supported catalyst Pd-BaTi demonstrating the potential of the former.

The catalytic coating

Three methods are employed to coat the EB-PVD PYSZ ceramic substrates with the La-based perovskite catalyst; the first method includes the previous synthesis of the perovskite applying the citrate route described in this study. Coating of the EB-PVD PYSZ ceramic substrates with the partially hydrolyzed gel of composition LaFeCo\textsubscript{0.3}-Pd leads to the formation of isolated perovskite agglomerates supported mainly on top of the EB-PVD PYSZ columns. The gaps between the EB-PVD PYSZ columns are not filled by applying this coating method leading to a very low perovskite loading on the surface of the PYSZ substrate.

The second coating method is carried out employing only the suspension containing La-based perovskite particles previously synthesized via the citrate route and pre-calcined at 500°C. This approach provides a coating with inhomogeneous thicknesses where the
perovskite particles are not really added to the PYSZ surface. The perovskite particles are deposited between the gaps of the EB-PVD PYSZ substrate whereas the column tips remain uncoated. This is the opposite to that microstructure obtained with the first coating method where most of the column tips are covered with the gel of the La-based perovskite.

To improve the quality of the La-based perovskite coatings on the EB-PVD PYSZ substrates, a third approach is carried out combining the observed advantages of the first two coating methods applied in this study. It combines the adhesion of the partially hydrolyzed perovskite observed in the first coating approach and the higher distribution degree achieved with the La-based perovskite particles alone. The coating method combining the two approaches mentioned above is classified as the best method employed in this study. Partially hydrolyzed gel of the perovskite acted as a “glue” between the previously synthesized and pre-calcined perovskite particles and also between the perovskite particles and the EB-PVD PYSZ substrate. Additionally, these coatings display a very good resistance during cyclic thermal shock ageing at 500° and 900°C. No phase(s) and morphological changes are observed upon thermal ageing at 500°C. The perovskite grains coated on the EB-PVD PYSZ surface start to migrate and grow after thermal cycling at 900°C. However, no significant crystal phase(s) changes of the coatings are observed after thermal ageing at this temperature. No mass gain or loss is registered after thermal ageing of the coatings LaFeCo(0.3)-Pd-EB-PVD PYSZ at 500° and 900°C demonstrating the stability of the perovskite crystals against cyclic thermal loading. The coatings LaFeCo(0.3)-Pd-EB-PVD PYSZ are tested for C₃H₆-SCR of NOₓ reduction but no activity is observed due to the low perovskite loading at the EB-PVD PYSZ substrates and to the low geometric surface area of the coatings. It is recommended to increase the geometric surface area for optimal catalytic testing of the coatings.

Catalytic coatings with higher geometrical surface than the coated EB-PVD PYSZ substrates are obtained by coating cordierite ceramic substrates with the La-based perovskite catalyst. The perovskite particles LaFeCo(0.3)-Pd are successfully coated on top of cordierite substrates provided by INTERKAT©. Colloidal silica is employed as a binder between the powder particles and the ceramic substrate, this method provided catalyst coatings with thickness of a few micrometers up to 20 μm. The coated cordierite substrates are catalytically tested for C₃H₆-SCR of NOₓ at high space velocities. In the presence of water vapour and high oxygen concentration (4.7 vol. %) a maximum 20 % of NOₓ-conversion is measured at ~450°C with the new catalytic converter. The powder based catalysts (the La-based perovskite alone) show slightly higher NOₓ-conversions at lower temperatures than the catalytic converter. In the catalytic converter the reactants must flow through the open channels and diffuse to the wall before they can react on the active sites. On the other hand the powder bed samples are supported between two plugs of quartz wool providing high contact surface between the catalyst and the gas phase resulting in improved NOₓ-conversions rates.