ZUSAMMENFASSUNG

Unter stationären Bedingungen lassen sich die hohen Umsatzraten moderner Drei-Wege-Katalysatoren (engl. three-way catalyst, TWC) auf die eingesetzten Platinmetalle (engl. platinum group metals, PGM) zurückführen, die als katalytisch aktive Komponente fungieren. Das transiente Umsatzverhalten wird jedoch von Speicher- und Freisetzungsprozessen von Sauerstoff sowie der Beschaffenheit des entsprechenden Speichermaterials dominiert. In der vorliegenden Arbeit werden auf dieser Basis vereinfachte kinetische Modelle abgeleitet, die eine genaue Beschreibung des dynamischen Verhaltens von Drei-Wege-Katalysatoren zulassen. Der Schlüssel zur Verhinderung von Emissionsdurchbrüchen nach dem Katalysator liegt in der Identifizierung und Aufrechterhaltung eines optimalen Oxidationszustands des Speichermaterials. Daher konzentrieren sich die entwickelten Modelle auf eine korrekte Beschreibung dieses örtlich veränderlichen Oxidationszustands. Ein wesentliches Element des entwickelten Einkanalmodells ist dabei die Zusammenfassung der im Abgas befindlichen Oxidations- und Reduktionsmittel zu entsprechenden Pseudokomponenten. Es wird dargelegt, dass es sich hierbei um eine sehr wirkungsvolle Vereinfachung handelt, die zu einem verbessersten Verständnis des dynamischen Umsatzverhaltens beiträgt. Zum Beispiel können Wechselwirkungen zwischen Sauerstoffspeichervorgängen sowie Edelmetallreaktionen unter verschiedenen Betriebsbedingungen und für unterschiedliche Alterungszustände des Katalysators auf einfache Art und Weise untersucht und beschrieben werden. Es wird gezeigt, dass zur Beschreibung des Umsatzverhaltens eines frischen Drei-Wege-Katalysators bei erhöhten Temperaturen eine explizite Berücksichtigung von Edelmetallreaktionen bei der Modellierung nicht notwendig ist und stattdessen eine implizite Berücksichtigung über die Beschreibung von Sauerstoffspeichervorgänge erfolgen kann. Die Zulässigkeit einer solchen Modellvereinfachung wird anhand der relativen Raten von Speicher- und Edelmetallreaktionen erläutert. Modellbasierte Untersuchungen dieser Art werden in der vorliegenden Arbeit für ein breites Spektrum von Abgaszusammensetzungen und Temperaturen durchgeführt. Dabei kommen insgesamt 17 Proben unterschiedlicher kommerzieller Katalysatoren zum Einsatz, die sich in Zusammensetzung und Alterungsgrad unterscheiden. Die entsprechenden Validierungsmessungen werden in einem isothermen Laborreaktor mit synthetischem Abgas durchgeführt und bieten damit genau definierte, vollständig reproduzierbare Testbedingungen. Die Abgaszusammensetzung am Einlass des Reaktors wird dynamisch variiert, um realistische Betriebsbedingungen eines TWC abzubilden. Um auf Grundlage der Messdaten Modellparameter zu bestimmen, wird ein robustes Optimierungsverfahren unter Berücksichtigung von Parametersensitivitäten und Parameteridentifizierbarkeit entwickelt. Dies erlaubt eine effiziente Entwicklung hochgenauer

und dennoch einfacher Modelle, die eine minimale Anzahl von Modellparametern beinhalten.

Aufgrund ihrer geringen Komplexität ist der Rechenaufwand für die Lösung der entwickelten Modelle im Allgemeinen gering, womit sie sich sowohl für die Online-Katalysatorregelung als auch für die Kopplung mit Echtzeithardware eignen. Hierbei kann es zielführend sein, abgesehen vom Beladungszustand des Katalysators auch Signale der typischerweise im Abgasstrang verbauten Lambdasensoren vorherzusagen. Folglich wurden entsprechende Sensoren im Messaufbau berücksichtigt und es werden einfache Anpassungsfunktionen vorgeschlagen, um deren Verhalten widerzuspiegeln.

Für den modellbasierten Entwurf von Regelungs- und On-Board-Diagnosestrategien ist es wünschenswert, das dynamische Verhalten verschiedener Katalysatoren auf systematische und aussagekräftige Art und Weise zu vergleichen. Die verwendete Parameteridentifizierbarkeitsanalyse stellt hierbei sicher, dass die entwickelten Modelle ausschließlich Parameter beinhalten, die eine hohe Aussagekraft bezüglich des Modellverhaltens besitzen. Gepaart mit einer geringen Gesamtanzahl von Parametern eignen sich die Modelle daher zur modellbasierten Charakterisierung und Selektion von Katalysatoren. Im Mittelpunkt steht dabei die Entwicklung geeigneter Methoden, um Unterschiede im dynamischen und stationären Verhalten verschiedener Proben schlüssig vergleichen und darzustellen zu können. Insbesondere für frische Proben wird gezeigt, dass die reversible Natur der Sauerstoffspeicher- und Freisetzungsreaktionen der Schlüssel zum Verständnis und zur korrekten Vorhersage des Sauerstoffspeicherfüllstands ist. Das Ausmaß, in welchem sich die Reaktionen im dynamischen Betrieb umkehren, ist für die getesteten Proben sehr unterschiedlich ausgeprägt. Es kann daher als charakteristischer Fingerabdruck der einzelnen Proben dienen.

Angesichts ihrer hohen Bedeutung für eine Emissionsminderung, werden Sauerstoffspeicherprozesse beim zyklischen Wechsel zwischen magerer und fetter Abgaszusammensetzung detailliert beleuchtet. Dies geschieht unter Berücksichtigung von Ortsprofilen der Modellzustände, gemessenen und simulierten Lambdawerten sowie Isotopenaustauschversuchen zur Beobachtung der Sauerstoffspeicherung aus Wassermolekülen. Während Alterungseffekte auf Grundlage qualitativer Trends diskutiert werden, kann die temperaturabhängige Kinetik und Thermodynamik der Speichervorgänge durch geeignete Funktionen abgebildet werden. Diese lassen eine genaue Vorhersage der Sauerstoffspeicher- und Lambdawerte im gesamten getesteten Temperaturbereich zu. Der Anstieg der dynamischen Speicherkapazität bei zunehmender Temperatur lässt sich gut durch einen sigmoidalen Kurvenverlauf beschreiben, der allerdings stark von der spezifischen Probe abhängt. Da die Gesamtspeicherkapazität im Modell als temperaturunabhängig angenommen wird, stellt sich der Kurvenverlauf allein über die im Modell hinterlegte Kinetik und Thermodynamik der Speichervorgänge ein.

Schlussfolgerungen zur Dynamik der Sauerstoffspeicherung, zu Alterungstrends oder zur Wechselwirkung von Edelmetall- und Speicherreaktionen werden in der vorliegenden Arbeit stets auf Basis der erhaltenen Modellierungsergebnisse getroffen. Um zu untersuchen, ob die Zusammenfassung von mehreren Abgaskomponenten zu wenigen Pseudokomponenten dabei zu unbegründeten Artefakten führt, werden zum Vergleich Rechnungen mit detaillierteren Modellen durchgeführt. Analog zum vereinfachten Modell bestehen die erweiterten Modelle aus einer Bilanz für den gespeicherten Sauerstoff sowie einer unterschiedlichen Anzahl an Materialbilanzen für die einzelnen Abgasspezies (wie Kohlenmonoxid, Wasserstoff, Kohlenwasserstoffe, Sauerstoff oder Stickoxide). Die erweiterten Modelle besitzen eine deutlich größere Anzahl an Parametern, die auf Basis der bereits für das vereinfachte Modell etablierten Methodik zur Parameteroptimierung für alle vorhandenen Proben anhand entsprechender Messdaten identifiziert werden. Im Gegensatz zum vereinfachten Modell beschränkt sich die Analyse auf eine Abgastemperatur von 450°C. Wie gezeigt wird, lässt sich so eine genaue Voraussage aller gemessenen Abgasspezies bei zyklischen Wechseln zwischen mageren und fetten Abgaszusammensetzungen erreichen.

Die für die vereinfachten Modelle beobachteten Trends werden mit Hilfe der erweiterten Modelle einer Überprüfung unterzogen. Erstens wird gezeigt, dass auch für die erweiterten Modelle eine explizite Beschreibung von Edelmetallreaktionen für gealterte Proben notwendig ist, während dies für frische Proben nicht zwingend erforderlich war. Zweitens wird gezeigt, dass die von einem erweiterten Modell vorhergesagten Beladungszustände denen des vereinfachten Modells ähnlich sind. Dies bestätigt die Gültigkeit des verwendeten Konzepts zur Vereinfachung der Modelle. Außerdem erlaubt es, die vom vereinfachten Modell vorhergesagten Beladungszustände unverändert in einem teilweise erweiterten Modell zu verwenden. Dies bringt einige Vorteile und interessante Anwendungsmöglichkeiten mit sich, die entsprechend diskutiert werden.

ABSTRACT

High steady-state conversion rates exhibited for modern three-way catalysts (TWCs) can be attributed to the platinum-group metals (PGMs) employed as catalytically active components. The transient conversion behavior, however, is dominated by oxygen storage and release processes and the nature of the corresponding storage material. The present work demonstrates how this can be exploited to construct simplified kinetic models that allow for accurately describing dynamic TWC operation. The key to preventing emission breakthroughs downstream of the catalyst is given by identifying and maintaining an optimal oxidation state of the storage material. Thus, the present work focuses on a correct assessment of the spatially distributed oxygen storage level. The developed one-dimensional single channel model lumps the oxidants and reductants present in the exhaust to corresponding pseudo-species. This is shown to represent a powerful concept for simplifying and understanding three-way catalysis. The lumping approach provides a basic understanding of the interaction of the storage material and the platinum group metals under different operating conditions and aging states of TWCs. It will be shown that storage and PGM reactions occur at similar rates whenever fresh catalyst samples are operated at elevated temperatures. This leads to a situation where explicitly modeling PGM reactions becomes redundant, allowing for a corresponding model reduction.

Throughout the thesis, similar model-based analysis and interpretation will be carried out for a broad range of exhaust compositions, temperatures, and a total of 17 commercial catalyst samples of different composition and aging state. The corresponding validation measurements are performed in an isothermal laboratory reactor with a synthetic exhaust, offering well-defined, fully reproducible test conditions. Dynamic excitations of the applied feed gas composition are used to closely resemble real exhaust conditions under dynamic operation. The employed exhaust gas analyzers are proven to be capable of well resolving the respective dynamics. In order to derive model parameters from the acquired measurement data, a robust model parameter optimization procedure has been developed, taking into account parameter sensitivity and identifiability analysis. This is shown to yield an efficient workflow for developing highly accurate yet simple models, which require a minimum number of model parameters.

Given their simplicity, the computational demand for solving the developed models is low, which qualifies them for online catalyst control as well as for coupling with real-time hardware. For such type of applications it is usually insightful to not only compute the catalyst storage level but to also predict the output of lambda sensors typically installed in the exhaust line. Consequently, corresponding sensors have been incorporated into the laboratory setup

and simple fitting functions are proposed for reflecting their behavior.

For model-based prototyping of control and on-board diagnosis strategies, it is desirable to be able to compare the dynamic behavior of different catalysts in a systematic and meaningful way. In that respect, the employed parameter identifiability analysis ensures that the developed models consist of meaningful parameters only. Together with a low number of parameters, the models are highly suitable for a model-based catalyst characterization and screening. Here, focus is put on developing appropriate methods for visualizing differences in the dynamic and steady-state behavior of various samples. Especially for fresh samples, the reversible nature of oxygen storage and release reactions is shown to be the key for understanding and correctly predicting oxygen storage levels under dynamic operation. The extent of reversibility is shown to be different for the tested samples. Therefore, it acts as a characteristic finger print of the specific sample.

Given the importance for catalyst control and emission abatement, the underlying processes during cycling between lean and rich exhaust compositions are analyzed in detail. This is done under consideration of spatial profiles of model states, measured and simulated lambda values, as well as isotopic exchange experiments designed to observe oxygen storage from water under dynamic operation.

The effect of temperature and catalyst aging on the model parameters is studied systematically, considering the confidence of the derived parameter estimates. While qualitative trends are discussed for the effect of aging, the obtained temperature trends in storage and release kinetics as well as thermodynamics are approximated by adequate functions allowing for an accurate prediction of oxygen storage levels and lambda values in the entire tested temperature range. The rise of dynamic storage capacity with increasing temperature is shown to be well reflected by sigmoidal-type functions and the shape of the functions is shown to strongly depend on the specific sample. Since the total storage capacity is assumed temperature-independent in the model, the rise of dynamic storage capacity is a result of the assumed oxygen storage kinetics and thermodynamics.

Throughout the thesis, modeling results are employed for deriving conclusions about the dynamics of oxygen storage, aging trends, or the relative importance of the platinum group metals and the storage material. To proof that the employed concept of lumping oxidizing and reducing agents in the exhaust does not affect the accuracy of the conclusions, extended models are considered as well. In analogy to the simplified model, they consist of a balance for the stored oxygen and of material balance equations for the individual exhaust gas species (such as carbon monoxide, hydrogen, hydrocarbons, oxygen, or nitrogen oxides).

The extended models have a much larger number of parameters. They are identified based

on the parameter optimization methodology already established for the simplified model. This is done for all available samples based on appropriate measurement data. In contrast to the simplified model, the analysis is limited to an exhaust gas temperature of 450°C. It is demonstrated that the evolution of all measured exhaust gas species during cycling between rich and lean exhaust gas compositions is accurately predicted by the models. Trends identified using the simplified model are reviewed using the extended ones. First, it is shown that the prerequisite of explicitly modeling PGM reactions for aged samples also holds for the extended models, while, again, this is not necessary for fresh samples. Second, it is shown that storage levels predicted by an extended model are similar to those of the lumped model. This confirms the validity of the concept used for model simplification. In addition, this allows for the storage levels predicted by the lumped model to be employed in an extended model without changes. Advantages and interesting applications for such type of modeling approach will be discussed.

1 Introduction

1.1 Three-way catalysts

The development of automotive exhaust catalysts was strongly driven by the Clean Air Act of 1970, a United States federal law, requiring a sharp reduction of carbon monoxide (CO), hydrocarbon (HC) and nitrogen oxide (NO_x) emissions from cars equipped with gasoline engines to improve air quality [41, 137]. While CO and HC where known to be efficiently converted with catalysts containing platinum-group metals (PGM) such as platinum (Pt), palladium (Pd), or rhodium (Rh) under an oxidizing atmosphere, selective NO_x reduction was known to take place over similar catalysts under reducing conditions. Early gasoline exhaust aftertreatment systems thus employed a dual-catalyst concept, where NO_x is eliminated over a first catalyst by operating the engine under slightly fuel-rich conditions and thereby maintaining a reductant (CO/HC) excess. This of course leads to an increased fuel consumption and the unconverted CO/HC has to be oxidized in a subsequent catalyst by secondary air injection in between the two catalysts [137, 138]. Soon it was however found that certain formulations of oxidation catalysts (containing mixtures of Pt/Rh) allow for the two processes to be combined in a single device, whenever the engine is run with a stoichiometric air-to-fuel ratio (AFR) [35, 138]. Based on the ability of such types of catalyst to simultaneously convert the three pollutants CO, HC, and NO_x, they are referred to as three-way catalyst (TWC).

Defining the lambda value as the ratio of the actual AFR to the stoichiometric AFR, optimal TWC efficiency is achieved only in a narrow operating window around $\lambda = 1$. During perturbations from this point to a fuel-rich mixture ($\lambda < 1$), a breakthrough of both CO and HC emissions occurs due to a lack of oxidants. Similarly, excursions to the lean side ($\lambda > 1$) lead to a breakthrough of NO_x emissions due to a lack of reductants. Due to the resulting prerequisite of maintaining a narrow operating window, the history of TWCs and their success is inevitably linked to the development of corresponding control strategies. Here, a key-enabler was the development of exhaust oxygen sensors and electronic fuel injection systems that be-

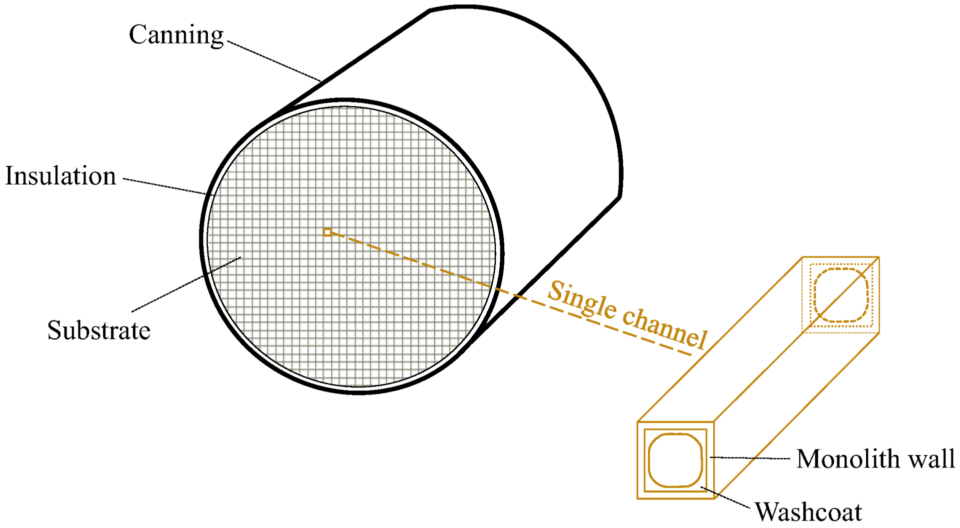

Figure 1.1 Typical layout of a three-way catalyst.

came available since the mid 1970s [46, 118]. Based on a Nernst voltage measured between a sensor electrode subjected to the exhaust and another one subjected to ambient air as a reference, it was possible to identify an oxygen excess or deficiency in the exhaust mixture entering the catalyst. This information could then be employed in an electronic control unit (ECU) to adjust the amount of fuel being injected by a feedback control scheme.

This combination of advances in catalyst design and control led to the first TWCs being successfully installed in gasoline cars in the late 1970s and an industry-wide adoption and dominance of TWC technology followed in the years thereafter until today [35, 40, 132]. The basic layout and working principle remained the same in the following 40 years of TWC research and development: As schematically presented in Fig. 1.1, typical TWCs are based on a honeycomb monolith structure made of cordierite which acts as a substrate for a coating process in which the active materials supported by a carrier such as aluminium oxide (Al_2O_3, alumina) are dispersed onto the monolith walls to form the so-called washcoat.

For a review of employed materials and preparation methods the reader is referred to [5, 40, 69, 99, 138]. The changes that have been performed in material design and selection over the years have been partly triggered by changes in fuel quality, material costs (i.e. PGM costs), and applied operating or control strategy. The predominant driver for developing advanced catalysts with high surface area, high thermal and mechanical stability, as well as high conversion efficiencies and high stability against PGM sintering and deactivation, however, was the progressively stringent emission legislation all over the world. To give an example that illustrates the substantial achievements: While the 1970 Clean Air Act NO_x tailpipe limit (the announced limits went into effect in 1975) was 3.1 grams per mile, an almost 10-fold decrease was reached by the mid 1990s and the lowest limits existing today in California are another order of magnitude lower, requiring conversion rates close to 100 percent [138, 139].

1.2 Oxygen storage materials

A decisive contribution to modern cars being capable of meeting today's emission limits was to overcome the inherent limitation of early TWCs to achieve high conversion rates only in a very narrow window around $\lambda = 1$. Already in 1976, Gandhi et al. recognized that a specific oxygen storage component had to be added to the washcoat of the catalyst for extending the operating window [41]. Subsequent storage and release of oxygen from this storage component can compensate for a temporary imbalance of oxidants and reductants in the exhaust and can avoid emission breakthroughs as long as the oxygen storage material is capable of either storing or releasing adequate amounts of oxygen fast enough. At that time, corresponding materials known to undergo subsequent oxidation and reduction during cycling of the air-to-fuel ratio around stoichiometry were different base metals and their corresponding oxides [41, 132]. However, cerium dioxide (CeO_2, ceria) was soon found to exhibit superior characteristics and remained the main oxygen storage component in TWCs until today. Despite of having many fields of application, its usage in the automotive industry represents the most important application of rare earth oxides with ceria being the most abundant one in the Earth's crust [67, 93].

The CeO_2 crystal lattice is characterized by the fluorite structure and can be produced by repeating the unit cell shown in Fig. 1.2 in three dimensions. In the face-centered-cubic (fcc) unit cell, the corner Ce^{4+}cations are each coordinated by eight oxygen anions while each

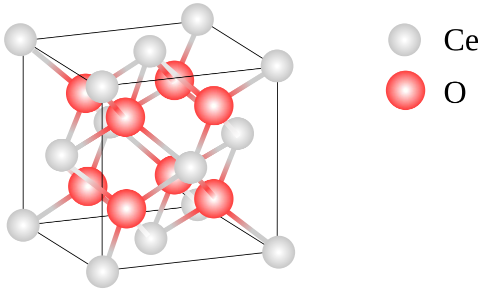

Figure 1.2 Unit cell of face-centered-cubic (fcc) CeO_2 crystal lattice.

oxygen anion forms a tetrahedron with its four neighboring Ce^{4+} cations [93]. The superior oxygen storage and release performance of the material is connected to its ability of forming non-stoichiometric $CeO_{2-\delta}$ phases when being reduced:

$$\mathrm{CeO_2} \underset{+\delta O}{\overset{-\delta O}{\rightleftharpoons}} \mathrm{CeO_{2-\delta}} \tag{1.1}$$

$$\mathrm{Ce^{4+}} \underset{+\delta O}{\overset{-\delta O}{\rightleftharpoons}} \mathrm{Ce^{3+}}\,. \tag{1.2}$$

The reduction process is accompanied by the formation of oxygen vacancies in the lattice and ceria ions changing its oxidation state from Ce^{4+} to Ce^{3+}. Further details regarding the obtained phases are summarized in [93]. The main advantage of ceria in TWCs is that the number of oxygen vacancies, that can be reversibly formed in the lattice, is high enough to allow for a sufficient buffering of air-to-fuel ratio perturbations. A corresponding quantitative measure is given by the oxygen storage capacity (OSC) of the material. First references of the now well established term are found in [41, 146]. Obviously, a high capacity is only beneficial if the kinetics of vacancy formation and refilling are fast enough to be in line with the frequency of typical air-to-fuel ratio oscillations. This led to the common practice of differentiating between a total and a dynamic oxygen storage capacity [134]. The former refers to the total oxygen uptake during an extended transition from a completely reduced to a completely oxidized state of the material and is usually measured by pulse or temperature programmed reduction or oxidation (TPR/TPO) experiments [69]. The latter, generally more useful for assessing TWC performance, refers to the oxygen uptake and release under typical transient driving conditions at realistic exhaust gas compositions. Early experimental evidence that ceria is indeed dynamically changing its oxidation state at a rate and to an extent that is relevant for improving TWC performance was presented by Herz et al. [55].

The addition of ceria in TWC washcoat formulations became common practice in the 1980s with technical improvements during that time focusing on achieving higher ceria content and higher dispersion on the alumina carriers, stabilized by dopants such as barium (Ba) or lanthanum (La) [40, 67, 93]. Apart from its most important role of allowing for oxygen storage and release, several other beneficial effects on TWC performance haven been associated with ceria [35, 67, 134, 138]:

- enhanced water-gas shift (WGS) and steam reforming (SR) activity, generating hydrogen under fuel-rich engine operation and thereby supporting NO_x reduction,
- improved and stabilized PGM dispersion,

- improved thermal stability of the alumina carrier,
- improved catalytic activity at PGM-CeO_2 interfaces.

Similarly, the presence of PGM was shown to highly improve the redox behavior of CeO_2, highlighting their mutual interaction [134].

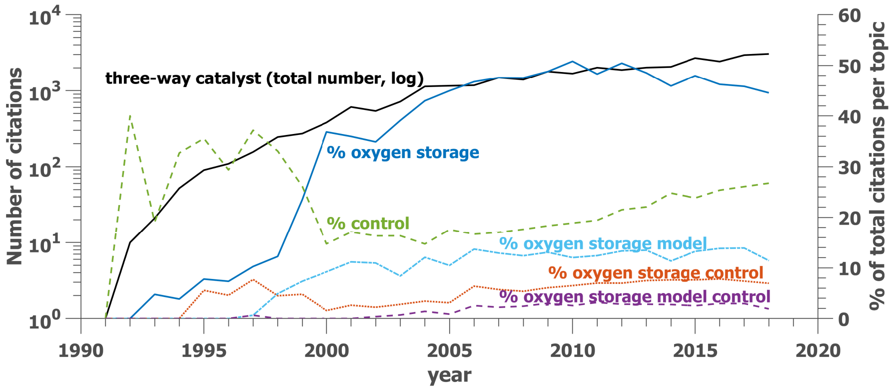

Figure 1.3 Overview of literature citations related to three-way catalysts. Source: Web of Science Core Collection, March 2019

Shortcomings of the CeO_2-based storage materials became apparent when focus was put on achieving better cold-start performance of TWCs in the 1990s. From a system design point of view, faster heat-up of the catalyst can be realized by shifting the catalytic converter closer to the engine. This is referred to as close-coupled catalyst and poses severe requirements on thermal stability of the employed materials [40, 67]. With temperatures in the TWC reaching 1000 °C, field aged catalysts exhibited increased PGM and ceria particle sizes as well as a decreased interface area between PGM and ceria, leading to insufficient activity [40].

This resulted in an extensive research effort to develop advanced OSC materials of improved thermal stability. While early publications on TWC and oxygen storage research are mainly found in commercial journals, a strong increase of related articles in the scientific literature can be observed from around 1990. To illustrate this, Fig. 1.3 depicts the total number of citations for “three-way catalyst” (applied search criteria) related articles based on the “Web of Science Core Collection” database as well as the percentage of these articles dealing with selected subtopics.

The already noted inseparability of TWC and control technology is well reflected by the high fraction of TWC publications dealing with control topics, especially in the early 1990s.

However, oxygen storage becomes the prevalent topic in the late 1990s, soon being a key topic in almost 50 percent of the cited articles.

Regarding the need of improving the thermal stability of conventional storage materials for close-coupled catalyst application, research focused on modifying ceria by additional components. Rather than creating simple physical mixtures, the ability of ceria to form single phase solutions with other oxides was employed to develop a new generation of storage components [93]. Here, zirconium dioxide (ZrO_2, zirconia) turned out to be the most efficient in terms of improving thermal stability [35, 67, 134]. As shown for ceria, ceria-zirconia $CeO_2 - ZrO_2$ mixed oxides can form non-stoichiometric phases when being reduced:

$$\mathrm{Ce_xZr_{1-x}O_2} \underset{+\delta O}{\overset{-\delta O}{\rightleftharpoons}} \mathrm{Ce_xZr_{1-x}O_{2-\delta}} \tag{1.3}$$

$$\mathrm{Ce^{4+}} \underset{+\delta O}{\overset{-\delta O}{\rightleftharpoons}} \mathrm{Ce^{3+}}\ , \tag{1.4}$$

where x represents the ceria content in the oxide. The amount of zirconia that can be dissolved in ceria is related to the elastic energy connected to replacing a Ce^{4+} by a smaller Zr^{4+} ion in the crystal lattice [93, 134] and, in practice, largely depends on the preparation technique [69, 132]. Apart from the modification of thermal durability, the so-called doping of Zr^{4+} was also shown to significantly improve the redox behavior and oxygen storage capacity of the material. This was generally explained by an improved O_2 mobility in the crystal structure, originating from the modifications of lattice strain and defect structure induced by the Zr-doping [87, 127, 134]. Since oxygen storage processes are mainly taking place near the surface of particles composed of pure CeO_2, oxygen transport in the bulk of ceria-zirconia solid solutions was shown to improve the storage capacity and kinetics of these materials [2, 40, 93].

Despite of hundreds of papers dedicated to understanding the redox behavior of ceria-zirconia based materials and trying to identify correlations between zirconia-content, textural properties, obtained phases, and oxygen storage performance (for example [29, 48, 58, 68, 141]), many details remain unclear [93]. This is partly due to thermodynamically unstable phases being formed in the temperature range relevant for TWC operation, making analysis of the materials difficult. Also, the redox behavior of the solid solutions has been shown to be highly sensitive to sample homogeneity and therefore to the applied preparation techniques, making comparisons amongst different samples difficult [66, 67]. Concluding, the extensive research efforts underline the importance of oxygen storage for the efficiency of three-way catalysts.

This is also reflected by the fact that the dynamic oxygen storage capacity is now generally employed as a measure for monitoring TWC activity in so-called on-board diagnosis (OBD) methods, where the air-fuel ratio is actively altered to estimate the oxygen uptake of the TWC under driving conditions [128]. This is achieved by a comparison of oxygen sensor signals upstream and downstream of the TWC. Besides of allowing for an OSC estimation, the second sensor is also employed for an improved air-fuel-ratio control, adapting the injected fuel amounts whenever perturbations from stoichiometry are observed. Such perturbations usually occur due to inaccuracies in controlling the air-fuel mixture entering the catalyst, leading to an oxygen excess or deficiency exceeding the buffering capability of the storage material which eventually results in a breakthrough of emissions. Such breakthroughs could be avoided when, instead of monitoring a sensor signal downstream the catalyst, the current oxygen storage level (OSL) inside the catalyst would be controlled. Although proposals for a direct measurement of the oxidation state can be found in literature [94], at present no commercially approved method exists. Thus, a model-based approach needs to be considered. As shown in Fig. 1.3, the development of corresponding oxygen storage models and their application in the control context have received increasing attention in the last years. As explained in the next section, the development of an efficient oxygen storage model is the main goal of the present work.

1.3 Thesis scope and outline

As discussed above, achieving high TWC performance requires to maintain an oxidation state of the oxygen storage material which avoids emission breakthroughs during air-fuel-ratio excursions either to the lean or rich side. In case deviations from an optimal level cannot be avoided, it is required to recover to that level in an optimal way from an emission perspective. For a system composed of an engine, air and fuel path, TWC, and exhaust line including sensors, this represents a complex optimization problem. In practice, it translates into finding suitable control algorithms and corresponding parameters for the electronic control unit (ECU). The corresponding development process requires extensive experimental testing and calibration, associated with high costs. This is especially true for a legislative environment, where testing for a wide range of boundary conditions is required (i.e. for real driving conditions). Here, model-assisted workflows generally offer a high potential for increasing efficiency. If all relevant parts of the system can be represented by corresponding models with high accuracy, development and testing of control algorithms as well as parameter tuning can be widely performed in a virtual environment and subsequent experiments are performed for validation purposes mainly. Obviously, the model quality itself depends on the experimental basis employed for model development. Thus, in practice, a compromise between model development effort and required experimental testing needs to be obtained.

Key element for a model-based development is a TWC model, capable of accurately describing oxygen storage dynamics. Simplicity and ease of parametrization are clearly desirable model properties, allowing for a low development and calibration effort. This in turn offers the possibility of model application at an early point in the development process, aiding catalyst suitability evaluation from a system and control perspective. Furthermore, control and on-board diagnosis algorithms need to cover not only the fresh state of the catalyst but also the full lifetime of the catalyst, that is, also aged samples. Here, simple models consisting of a relatively low number of parameters can be more easily recalibrated to reflect the aging state. Also, correlations between the aging state of a given TWC and corresponding model parameters can be more easily obtained for simple models with a low number of parameters. If model parameters can be uniquely identified from a given experimental data set or sensor readings, meaningful correlations between the aging state and model parameters can be obtained. This allows for deriving models of the aging process and generally permits a model-based catalyst characterization or screening covering the whole lifetime. As simple models are usually less demanding from a computational point of view, they offer advantages when the simulation environment requires execution of the models in real-time. This can be the case when models are coupled with real-time hardware such as the ECU or when the models are executed on the ECU itself for online control purposes. Here, it can be of course highly advantageous if the models executed on the ECU are identical to the ones used in the development process.

In this context, the present work is designated to developing a simplified, chemically motivated TWC model, focusing on correctly describing oxygen storage processes for a broad range of realistic operating conditions and commercial TWC samples, both in fresh and aged state. Given the complexity of analyzing TWC behavior in a system of active control loops and dynamically changing temperature, flow, and exhaust composition, the present work, as a first step, focuses on analyzing various TWC samples in a laboratory reactor under a synthetic exhaust, offering well-defined, fully reproducible test conditions. The goal is here to better understand oxygen storage dynamics and to incorporate these insights into a corresponding model. Keeping the above mentioned points regarding a model-based development in mind, the scope of the thesis is to derive an efficient model calibration workflow, yielding models consisting of meaningful parameters only.

Given the scope of the thesis, the following outline is derived:

- Chapter 2 discusses general relations between oxygen storage, exhaust gas composition, and lambda value, which are essential for understanding TWC behavior. Based on these relations, the concept of lumping certain exhaust gas species in order to simplify three-way catalysis is being introduced. This represents a key element for the model development process described in this work.

- Chapter 3 describes the experimental setup and performed measurements for characterizing the employed three-way catalyst samples. It addresses the capability of the setup to measure realistic TWC dynamics under fast changes in the inlet exhaust composition. This requires exhaust analyzers with the capability to resolve these dynamics. The dynamics of oxygen sensors installed in the exhaust line are being analyzed and simple functions are proposed to represent the sensor output. Regarding the obtained measurement results, the focus lies on highlighting important aspects of dynamic TWC behavior for both fresh and aged catalysts in order to set a framework for the model development.

- Chapter 4 reviews detailed and simplified three-way catalyst models proposed in literature and summarizes how they approach the description of oxygen storage processes. It is outlined how the corresponding insights are employed for the development of the model used in the present work. The model structure and parameters are then analyzed in order to facilitate the interpretation of modeling results presented later.

- Chapter 5 discusses how to derive model parameters from the acquired measurement data. Focus is put on describing the methods applied for assessing the identifiability of model parameters. Based on a given parameter optimization result, this type of analysis is frequently employed in the present thesis to derive a subset of uniquely determined model parameters. This information is then employed for model reduction.

- Chapter 6 discusses model optimization, corresponding results, and model validation for dynamic TWC operation at a constant temperature but under an exhaust gas composition that cycles between a wide range of lean and rich lambda values. It gives a detailed description of important effects during transitions between a lean and rich exhaust composition and shows how the model can be employed to better understand these effects. Differences in the dynamic behavior between various fresh catalyst samples as well as the effect of aging are explained in detail and the corresponding implications for the model parameters are being discussed. Here, it is explained why platinum group metal reactions need to be explicitly considered for modeling the behavior of aged samples and why they do not need to be considered for fresh samples.

- Chapter 7 is structured similar to chapter 6. However, rather than analyzing TWC operation for a wide range of lambda values, the dynamic excitation of the inlet exhaust composition is kept constant in order to independently analyze and model the effect of temperature on TWC dynamics. Inherent limitations of the applied modeling approach in terms of capturing light-off behavior are being discussed.
- Chapter 8 presents model extensions and corresponding modeling results that further proof the validity of the employed modeling approach as well as the conclusions drawn in chapter 6. That is, it shows how the concept of lumping certain exhaust gas species can either be fully or partially reversed in a systematic manner. Also, important aspects of such an approach for model application are being discussed.

Parts of chapters 3 to 6 have already been published in [13].

2 Lambda value, oxygen storage, and lumped concentrations

The following chapter has three objectives. First, a definition of the lambda value will be derived that will be used frequently throughout this thesis. Second, a connection between λ and oxygen storage effects will be established. Third, it will be shown that the concept of lumping certain exhaust gas species can be insightful for analyzing oxygen storage processes in three-way catalysts.

To meet the objectives, it is helpful to show how λ can be defined along a typical exhaust line of a spark-ignition engine (Fig. 2.1). The mass flow of air entering the engine is usually measured by a hot-film air-mass meter (HFM) and can be controlled by a throttle valve. In general, λ can be defined based on the air-fuel ratio (AFR) resulting from the injection of a given amount of fuel into the combustion chamber:

$$\lambda = \frac{\mathrm{AFR}_{\mathrm{actual}}}{\mathrm{AFR}_{\mathrm{stoichiometry}}} = \frac{\frac{\dot{\mathrm{M}}_{\mathrm{air,actual}}}{\dot{\mathrm{M}}_{\mathrm{fuel}}}}{\frac{\dot{\mathrm{M}}_{\mathrm{air,stoichiometry}}}{\dot{\mathrm{M}}_{\mathrm{fuel}}}} = \frac{\dot{\mathrm{M}}_{\mathrm{air,actual}}}{\dot{\mathrm{M}}_{\mathrm{air,stoichiometry}}} = \frac{\dot{\mathrm{M}}_{\mathrm{O_2,actual}}}{\dot{\mathrm{M}}_{\mathrm{O_2,stoichiometry}}} \,. \tag{2.1}$$

It is very important to note that in this definition, the actual amount of oxygen being present in the exhaust ($\dot{\mathrm{M}}_{\mathrm{O_2,actual}}$) is always compared to the amount of oxygen needed for stoichiometric combustion of a given fuel ($\dot{\mathrm{M}}_{\mathrm{O_2,stoichiometry}}$). While the denominator therefore always refers to engine-in (EI) conditions, the numerator can refer to the gas composition at any given position. Assuming that the engine is run with a fuel of the composition $\mathrm{CH_x}$ and dry air only, oxygen is solely present in its elemental form in the EI position. Thus, the actual amount of oxygen present can be directly deduced from the air mass flow measurement:

$$\dot{\mathrm{M}}^{\mathrm{EI}}_{\mathrm{O_2,actual}} = \omega_{\mathrm{O_2,air}}\,\dot{\mathrm{M}}_{\mathrm{air}} \,, \tag{2.2}$$

where $\omega_{\mathrm{O_2,air}}$ represents the mass fraction of oxygen in air. Neglecting oxygen sinks or sources in the engine, the engine-out (EO) mass flow of oxygen equals the EI mass flow of oxygen.

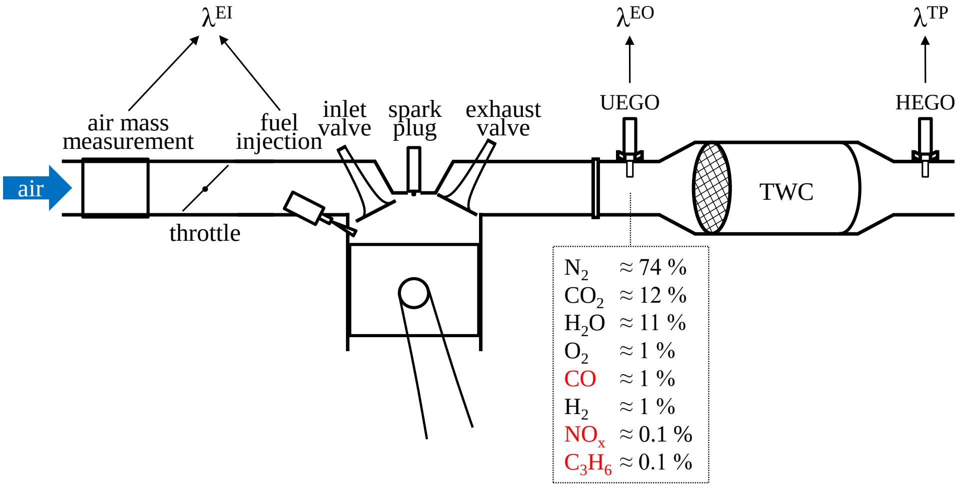

Figure 2.1 Sketch of a typical exhaust line of a spark-ignition engine.

Together with equation (2.1), this leads to the result:

$$\lambda^{\mathrm{EO}} = \lambda^{\mathrm{EI}} \, . \tag{2.3}$$

However, in the EO position, oxygen may be present both in its elemental form or bound to different exhaust gas species produced during the combustion of the fuel $\mathrm{CH_x}$ with air. For simplicity, air is assumed to be composed of oxygen and nitrogen only and the respective combustion reaction is presented in an unbalanced form:

$$\mathrm{CH_x} + \mathrm{O_2} + \mathrm{N_2} \longrightarrow \mathrm{CO_2} + \mathrm{H_2O} + \mathrm{CO} + \mathrm{H_2} + \mathrm{C_3H_6} + \mathrm{NO} + \mathrm{NO_2} \, . \tag{2.4}$$

Typical orders of magnitude for the concentrations of the different reaction products and unconverted oxygen are depicted in Fig. 2.1. Throughout this thesis, hydrocarbons produced during the combustion process will be represented by $\mathrm{C_3H_6}$. Regarding nitrogen oxides, only NO and $\mathrm{NO_2}$ will be considered. Given the oxygen-containing reaction products from reaction (2.4), the EO oxygen mass flow can be calculated from:

$$\dot{\mathrm{M}}_{\mathrm{O_2,actual}} = 0.5\,\mathrm{MW_{O_2}}\left(2\dot{\mathrm{N}}_{\mathrm{O_2}} + \dot{\mathrm{N}}_{\mathrm{NO}} + 2\dot{\mathrm{N}}_{\mathrm{NO_2}} + 2\dot{\mathrm{N}}_{\mathrm{CO_2}} + \dot{\mathrm{N}}_{\mathrm{H_2O}} + \dot{\mathrm{N}}_{\mathrm{CO}}\right) . \tag{2.5}$$

The exact composition of the exhaust gas exiting the engine is dependent on a variety of parameters influencing the combustion process. While the reader is referred to [56] for a detailed analysis, some general trends will be briefly discussed based on Fig. 2.2. Although absolute quantities are depicted in the figure, the focus lies on visualizing the general dependency of the EO exhaust gas composition on λ^{EI}.