Oxygen storage dominated three-way catalyst modeling for fresh catalysts

J. Bickel[a,*], B. Odendall[b], G. Eigenberger[a], U. Nieken[a]

[a] Institute of Chemical Process Engineering, Stuttgart, Germany
[b] AUDI AG, Ingolstadt, Germany

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ABSTRACT

Meeting future legislations for the emissions of spark-ignition engines requires the development of efficient three-way catalyst (TWC) models. These models can both be employed for online catalyst control as well as model-based development of control and on-board diagnosis (OBD) strategies. In this paper we present such a model that aims at capturing transient TWC dynamics of fresh catalysts at elevated temperatures. Applying a parameter subset selection strategy, we demonstrate that solely taking into account the dynamics of oxygen storage and release is sufficient for this purpose and reactions associated with processes taking place on the platinum-group metals do not have to be modeled explicitly. The one-dimensional single channel model lumps the exhaust gas species into two pseudo components, one being able to oxidize and one being able to reduce the oxygen storage material. The respective reaction kinetics are considered reversible with non-linear functions depending on the oxidation state of the material being put in the center of focus. Model validation is carried out using experimental data from an isothermal synthetic gas test bench. The applied feed gas composition closely resembles real exhaust conditions under dynamic operation. By employing local parameter sensitivity and identifiability analysis and investigating the differences between a total of five fresh catalysts from different commercial suppliers, we propose a set of only five parameters that can be used to accurately model oxygen storage and release dynamics under isothermal conditions. The results emphasize the importance of accounting for oxygen storage from water as well as the need of using a spatially distributed model. Apart from the above mentioned applications, the model is shown to be suitable for fast catalyst screening and characterization.

1. Introduction

Provided that a spark ignition engine is operated with a stoichiometric air-to-fuel ratio (AFR), and the exhaust catalyst is operated at temperatures above light-off, a three-way catalyst (TWC) is then able to simultaneously reduce the emissions of carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NO_x) with very high conversion rates. Defining the lambda value as the ratio of the actual AFR to the stoichiometric AFR, this operation point is characterized by $\lambda=1$. 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.

A decisive step in more than 30 years of TWC development, driven by increasingly stringent emission legislations, was the incorporation of an oxygen storage material into the washcoat of the catalyst. Subsequent storage and release of oxygen from this material can compensate for a temporary imbalance of oxidants and reductants in the exhaust and can avoid breakthroughs as long as the oxygen storage

material is capable of either storing or releasing adequate amounts of oxygen fast enough. The conversion efficiency of the TWC is consequently dependent on the oxygen storage capacity (OSC), the storage and release kinetics, and the current oxidation state of the material. The preparation of catalysts that are able to store and release oxygen very efficiently has been the subject of extensive catalyst research (Kašpar and Fornasiero, 2003). However, during engine operation, the actual oxidation state of the storage material is still inaccessible to direct measurement. Automatic observation and engine control tools are therefore required which have to be based upon efficient and easy to implement models of the catalyst storage dynamics. At the same time, these models can be employed for a model-based development of control and OBD strategies. The development of a corresponding model is the topic of the present contribution.

Present storage materials are based upon ceria-zirconia mixed oxides, modified by various additional components. The OSC of these materials arises from the ability of ceria ions to cycle between the two different oxidation states Ce^{4+} and Ce^{3+}. The details of oxygen storage and release dynamics in TWCs are complicated by the fact that oxygen

stored near the surface of ceria-zirconia particles is readily accessible, while bulk storage and release processes are slower. It is therefore common practice to differentiate between a total and a dynamic oxygen storage capacity. 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 TPR/TPO experiments. The latter is connected to the oxygen available under typical transient driving conditions and realistic exhaust gas compositions (Boaro et al., 2004). The task of controlling the oxidation state during TWC operation therefore requires to determine an effective oxygen storage level (OSL) and develop adequate control strategies. Although proposals for a direct measurement of the oxidation state can be found in literature (Moos, 2010), presently no commercially approved method exists.

As a result, numerous model-based approaches have been studied in literature. They rely on the signals of conventional exhaust gas oxygen (λ) sensors (EGO). Clearly, their success is highly dependent on how the applied TWC models consider the oxygen storage and release dynamics. In order to classify the proposed models, they can be differentiated in a first step into chemically motivated (Aimard et al., 1996; Auckenthaler, 2005; Bekiaris-Liberis et al., 2012; Kiwitz et al., 2012; Kumar et al., 2012, 2014) and rather empirical ones (Shafai et al., 1996; Peyton Jones et al., 1999, 2000; Brandt and Wang, 2000; Balenović et al., 2001, 2006; Muske et al., 2008). The models explicitly accounting for chemical reactions are generally employing a single-channel model of the TWC and apply the concept of lumping certain exhaust gas species. More specifically, oxidizing agents such as NO_x and O_2 are lumped into a pseudo species OA while reducing agents such as CO, HC, and H_2 are lumped into a pseudo species RA. The products of reducing agent oxidation (H_2O/CO_2) are lumped into a pseudo species RAO. The models can be further classified using the set of selected features shown in Table 1.

Short explanations for the listed features will be given in the following:

- Exhaust species: based on the assumption that their dynamic behavior is similar, certain exhaust gas species are being lumped. This column lists the species that are considered in the mass balance equations of the specific model. Most models assume the H_2O/CO_2 concentration to be constant. And some treat hydrogen as an individual component not being lumped into the RA concentration.
- Qs gas phase: based on the assumption that gas phase dynamics are much faster as opposed to oxygen storage dynamics, the models neglect mass accumulation in the gas phase and consequently apply the quasi-steady (qs) state assumption to the gas phase.
- Stored species: the species being able to accumulate in the specific

model are listed in this column. Usually, oxygen is assumed to be the only species being stored in the catalyst.
- PGM: besides of reactions leading to a change of the oxygen storage level, the model accounts for global reactions that are associated with processes taking place on the platinum-group metals (PGM) in the washcoat of the catalyst.
- O from RAO: the model takes into account that H_2O and/or CO_2 is able to oxidize ceria.
- 1-D: a spatially distributed model is proposed (rather than an integral model).
- Mass transfer: the column indicates whether the model explicitly accounts for external (ext) mass transfer effects in the channel of the TWC or internal (int) mass transfer effects in the washcoat of the TWC.

As a general requirement, the model should be sufficiently accurate but at the same time of low complexity in order to be easily implemented in current engine control systems. Besides of the description of mass and heat transfer phenomena, a major source of complexity in TWC models is given by the description of oxygen storage processes. Since the experiments presented in this work were conducted under isothermal conditions and at a single temperature, we focus our discussion on the development and validation of a corresponding kinetic model rather than a reactor model and thereby rely on various model features already presented in literature (Table 1). Combining novel ways of formulating and analyzing reaction rate expressions commonly used in TWC models with an efficient parameter optimization and subset selection procedure, we present an efficient workflow for the development of a model complying with the before mentioned requirements and demonstrate its suitability for catalyst characterization.

2. Experimental

As indicated, the experiments should provide realistic and reproducible conditions for the evaluation of the derived model, concerning its application in engine control. This means that commercial TWC catalysts from different suppliers have to be tested under identical conditions with a simulated exhaust which is close to that of actual TWC equipped engines. For the experiments, an isothermal so-called flat-bed reactor test bench has been used which has already been demonstrated to be a practicably useful tool for this purpose (Brinkmeier et al., 2005).

2.1. Setup

A simplified flow chart of the experimental setup is shown in Fig. 1.
To investigate oxygen storage dynamics, two thin slices (each one channel row high) of the respective monolith catalyst are placed in the flat-bed reactor channel. Isothermal conditions are sustained through temperature controlled heating of the reactor top and bottom plate. The feed gas consists of a constant flow of 12 (vol)% CO_2 and 11% H_2O, 0.11% C_3H_6 and 0.1% NO in N_2. This flow is provided by the dry gas flow ("main") and the pure water vapor flow ("H_2O") shown in Fig. 1. To allow for dynamic (step) changes between fuel lean and rich conditions, two additional feeds, "high" and "low" with different amounts of CO, H_2, O_2, and N_2 are alternately added to the main flow.

While the flow rates of the dry gases are controlled by mass-flow controllers (MFC), the constant water vapor stream is produced by a capillary evaporator, fed by a (pulse-free) HPLC pump (Freund et al., 2006). Four switch valves allow for step changes between rich and lean. Pressure control at the reactor exit and in the "waste" line provide constant flows also during switches. The feed gas entering the reactor passes a static mixer (triangle) and can then be withdrawn at different positions for mass spectrometer (MS) analysis.

Table 1
Classification of various chemically motivated control-oriented TWC models proposed in literature.

Model	Exhaust species	Qs gas phase	Stored species	PGM	O from RAO	1-D	Mass transfer
Aimard et al. (1996)	OA, RA		O	✓			
Auckenthaler (2005)	OA, RA, H_2	✓	O, RA		✓	✓	ext
Bekiaris-Liberis et al. (2012)	OA, RA, (H_2)		O			✓	
Kiwitz et al. (2012)	OA, RA, RAO	✓	O		✓	✓	
Kumar et al. (2012)	OA, RA		O	✓			ext+int
Kumar et al. (2014)	OA, RA		O	✓		✓	ext+int
this work	OA, RA	✓	O	✓	✓	✓	