



# Is oxygen storage in three-way catalysts an equilibrium controlled process?

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## ABSTRACT

Existing reaction mechanisms for three-way catalysts ignore the oxidation of Ce<sub>2</sub>O<sub>3</sub> by H<sub>2</sub>O or CO<sub>2</sub> and therefore treat oxygen storage on ceria as a kinetically controlled non-equilibrium process. Such mechanisms do not correctly reproduce a number of practically important phenomena.

Based on transient concentration step experiments, this paper demonstrates that the oxidation of reduced ceria by H<sub>2</sub>O or CO<sub>2</sub> plays an important role for the understanding of the oxygen storage dynamics. The results of the step experiments are well reproduced by a simple three-reaction kinetic model that takes into account the equilibrium character of oxygen storage.

There are a number of effects that cannot be understood based on the conventional non-equilibrium mechanisms:

- The oxygen storage capacity is lowered by the presence of H<sub>2</sub>O and CO<sub>2</sub>.
- The oxygen storage capacity depends on the amplitude of the lambda-oscillations.
- Following a rich-lean step the catalyst emits CO/H<sub>2</sub> when there is no CO/H<sub>2</sub> in the inlet.
- Delayed CO/H<sub>2</sub> emissions in the so-called fuel cut-off scenario.
- The capability of the oxygen storage to dump lambda-oscillations, even if the average lambda is slightly rich.

All these effects are explained and quantitatively predicted by the equilibrium based oxygen storage model.

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## 1. Introduction

Three-way catalysts are today's most successful exhaust after treatment system for gasoline engines. With a warmed up catalyst and at steady state conditions conversions of more than 95% are reached for the three pollutants CO, NO and HC.

Transient engine operation, such as accelerations, unavoidably causes temporary deviations from a stoichiometric exhaust composition. For this purpose three-way catalysts contain ceria compounds that act as an oxygen buffer [1]. During rich excursions ceria is reduced by CO or H<sub>2</sub>:



During a lean phase, the reduced ceria is reoxidized by oxygen:



In a modern vehicle the air-to-fuel ratio  $\lambda$  is controlled by a cascaded feedback control algorithm with one  $\lambda$  sensor upstream and a second sensor downstream of the catalyst. The operation of the controller and especially the behavior of the second lambda sensor are strongly influenced by the oxygen storage dynamics. For this reason a detailed understanding of the oxygen storage chemistry is necessary for the development of improved lambda control schemes and appropriately adapted catalyst formulations.

In the literature one finds a large number of kinetic models for three-way catalysts. These range from relatively simple models with a small number of global reactions [2–5] to mechanistic models based on a large number of elementary surface reactions [6–15]. Table 1 summarizes the oxygen storage related reactions for some widely used reaction mechanisms. Surprisingly, none of these mechanisms takes into account the oxidation of Ce<sub>2</sub>O<sub>3</sub> by H<sub>2</sub>O or CO<sub>2</sub> (the reverse reactions of reactions (1) and (2)). Therefore, existing mechanisms do not treat the reduction reactions (1) and (2) as equilibrium reactions. One exception is the mechanism by Auckenthaler et al. [12], where the oxidation of ceria by H<sub>2</sub>O has been implemented as part of the water gas shift reaction mechanism.

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## Nomenclature

$A_{\text{cat}}$	specific catalytic active surface ( $\text{m}^{-1}$ )
$A_{\text{geo}}$	specific geometric catalyst surface ( $\text{m}^{-1}$ )
$A_i$	pre-exponential factor of reaction $i$ ( $\text{s}^{-1}$ )
$c_i$	concentration of species $i$ in the channel ( $\text{mol}/\text{m}^3$ )
$c_{\text{pg}}$	specific heat capacity of the gas phase ( $\text{J}/(\text{kg K})$ )
$c_{\text{ps}}$	specific heat capacity of the solid phase ( $\text{J}/(\text{kg K})$ )
$D_{\text{chan}}$	diameter of the channel (m)
$D_{\text{wc}}$	washcoat thickness (m)
$k_{c,i}$	mass transfer coefficient from the gas phase to the surface of the species $i$ (m/s)
$E_i$	activation energy of reaction $i$ (J/mol)
$H_i$	enthalpy of species $i$ (J/mol)
$k_i$	reaction rate constant of reaction $i$ ( $\text{s}^{-1}$ )
$K_i$	equilibrium constant of reaction $i$
$L$	storage capacity per active surface ( $\text{mol}/\text{m}^2$ )
$\dot{m}$	mass flow (kg/s)
$M_i$	molar mass of species $i$ (kg/mol)
$\bar{M}$	average molar mass of the mixture (kg/mol)
$\nu_{i,j}$	stoichiometric coefficient of species $i$ in reaction $j$
$p_{\text{exh}}$	pressure in the catalyst (Pa)
$r_i$	reaction rate of reaction $i$ ( $\text{s}^{-1}$ )
$R$	universal gas constant ( $\text{J}/(\text{mol K})$ )
$\dot{s}_t$	reaction source term of species $i$ ( $\text{s}^{-1}$ )
$T_{\text{g}}$	temperature of the gas phase (K)
$T_{\text{s}}$	temperature of the solid phase (K)
$x_i$	concentration of species $i$ in the washcoat ( $\text{mol}/\text{m}^3$ )
$\alpha$	heat transfer coefficient from the solid to the gas phase ( $\text{W}/(\text{m}^2 \text{K})$ )
$\varepsilon_{\text{g}}$	volume fraction of the gas phase
$\varepsilon_{\text{wc}}$	washcoat porosity
$\lambda$	air-to-fuel ratio
$\lambda_{\text{g}}$	heat conductivity of the gas phase ( $\text{W}/(\text{m K})$ )
$\lambda_{\text{s}}$	heat conductivity of the solid phase ( $\text{W}/(\text{m K})$ )
$\rho_{\text{g}}$	density of the gas phase ( $\text{kg}/\text{m}^3$ )
$\psi_{\text{Ce}_2\text{O}_4}$	relative oxygen storage level on the ceria
$\sum \nu_i$	diffusion volume of species $i$ in $N^2$ ( $\text{cm}^3/\text{mol}$ )

The fact that reduced ceria can be oxidized by  $\text{H}_2\text{O}$  or  $\text{CO}_2$  is well known in the literature. Otsuko et al. [16] observed both reactions and found that  $\text{H}_2\text{O}$  oxidizes  $\text{Ce}_2\text{O}_3$  much faster than  $\text{CO}_2$ . The oxidation of  $\text{Ce}_2\text{O}_3$  by  $\text{CO}_2$  has also been reported by Sharma et al. [17]. The reaction of ceria with mixtures of  $\text{H}_2/\text{H}_2\text{O}$  or  $\text{CO}/\text{CO}_2$  has been used for the experimental determination of the ceria reduction thermodynamics [18–21]. Furthermore, the reactions of  $\text{Ce}_2\text{O}_3$  with  $\text{H}_2\text{O}$  and  $\text{CO}_2$  are discussed to play an important role in the processes for water gas shift, steam reforming and fuel reforming [22]. Padeste et al. studied the effect of water on the oxygen storage capacity and found that the storage capacity is reduced in the presence of water [23].

Despite the fact that the reactions of  $\text{Ce}_2\text{O}_3$  with  $\text{H}_2\text{O}$  and  $\text{CO}_2$  are well known in the literature, it seems that the role of these reactions for the understanding of the oxygen storage dynamics in three-way catalysts has not been sufficiently investigated. This statement is supported by the fact that these reactions are not included in the published reaction schemes.

Three-way catalysts, when exposed to dynamic operating conditions, show a number of effects that cannot be understood in

terms of the existing non-equilibrium oxygen storage reaction mechanisms:

- The observed oxygen storage capacity is lower in the presence of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ .
- The observed oxygen storage capacity depends on the  $\text{CO}/\text{H}_2$  concentrations.
- When the catalyst is exposed to a rich-lean step the outlet remains rich for some time after the inlet has switched to lean. This means that the catalyst emits  $\text{CO}$  and  $\text{H}_2$  when the inlet only contains  $\text{H}_2\text{O}$  and  $\text{CO}_2$ .
- When a beforehand oxidized catalyst is subjected to a short rich pulse followed by stoichiometric operation, the catalyst emits a delayed pulse of  $\text{CO}/\text{H}_2$  during the stoichiometric phase.
- When a catalyst is operated with an oscillating air-to-fuel ratio at slightly rich conditions the oscillations are adsorbed by the oxygen storage.

The purpose of this paper is to show that all these effects can be understood, if the equilibrium character of the oxygen storage reactions (1) and (2) is taken into account. In a first step the importance of the reverse reactions (–1) and (–2) is demonstrated in a series of pulse experiments. These experiments are used to parameterize a simple three-reaction equilibrium oxygen storage model.

In a second step the so far unexplained effects are reproduced in model-gas experiments and it is shown that all effects are explained and predicted by the equilibrium oxygen storage model.

## 2. Methodology

### 2.1. Experimental

The measurements for this investigation were performed on a model-gas test bench, where the exhaust gas is mixed from bottles and heated up to the desired temperature. The gas mixing system of the test bench is optimized to have a fast continuous  $\lambda$  adjustment with time constants comparable to an engine test bench. The time constant and transport delay, measured with lambda steps and a wide-range  $\lambda$  sensor, are both on the order of 150 ms. The experimental setup has been described in more detail in [24].

For the measurement of  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{N}_2$  the test bench is equipped with a Pfeiffer Omnistar mass spectrometer that is optimized for fast response measurements. The five measured atomic masses can be scanned in less than 60 ms. Very thin and short capillaries reduce the time delay of the modified inlet system to approximately 80 ms.  $\text{CO}$  is measured using an Airsense Compact mass spectrometer.

The inlet concentrations are recorded using the mass flow sensor signals of the flow controllers.

The catalyst used in this investigation is a commercial three-way catalyst containing a ceria/zirconia mixed oxide oxygen storage compound. The precious metal loadings are 1 g/ft<sup>3</sup> rhodium, 8 g/ft<sup>3</sup> palladium, and 1 g/ft<sup>3</sup> platinum. The catalytically active material is coated on a cordierite monolith with a cell density of 600 cells per square inch. Measurements were performed on an aged (8 h 985 °C in air) sample with a diameter of one inch and a length of 3 in.

### 2.2. Numerical model

The catalytic monolith is modeled as a single one-dimensional and adiabatic channel. Radial heat and concentration gradients between different channels are neglected. The model consists of two gas phases and one solid phase. The first gas phase takes into

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