Effect of propene, propane, and methane on conversion and oxidation state of three-way catalysts: a microwave cavity perturbation study

Gregor Beulertz [a,b], Martin Votsmeier [b,*], Ralf Moos [a,*]

[a] Bayreuth Engine Research Center, Department of Functional Materials, University of Bayreuth, 95445 Bayreuth, Germany
[b] Umicore AG & Co. KG, 63403 Hanau-Wolfgang, Germany

ABSTRACT

This paper presents laboratory reactor measurements of the steady-state conversion of the pollutants CO, hydrocarbons and NO over a three-way catalyst containing ceria as an oxygen-storage component. It is shown that the presence of the saturated hydrocarbons C_3H_8 or CH_4 causes a shift in the stoichiometry of optimal conversion (CO–NO crossover) to fuel-rich compositions. The shift was more pronounced at lower temperatures and can be explained by the kinetic limitation of the hydrocarbon oxidation reaction. A microwave cavity perturbation technique was used to measure *in situ* the oxidation state of the ceria. In a first step, titration experiments were performed. The oxygen-storage level was adjusted to a predefined level by equilibration with a H_2/H_2O mixture. The experiments showed that for a given temperature, the microwave-derived signal (here the resonance frequency) correlates well with the oxidation state of ceria. The microwave cavity perturbation technique was then applied simultaneously to steady-state performance tests in the presence of different hydrocarbons. It was found that if the exhaust stoichiometry is ramped from lean to fuel rich, the CO–NO crossover point in all cases coincides with a strong decrease in the oxidation state of ceria. The correlation between the oxidation state of the catalyst and the catalytic performance is found to be independent of the catalyst temperature and the nature of the hydrocarbon. The CO–NO crossover point can be precisely determined by the microwave cavity perturbation technique. The results suggest that a microwave-based measurement may, under some circumstances, allow for a more precise control of the catalyst performance than the conventional control by lambda sensors.

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1. Introduction

The conversion of the three-way catalysts (TWC) strongly depends on the stoichiometry of the exhaust mixture. In a narrow range of exhaust stoichiometry, the catalyst simultaneously converts NO, CO and hydrocarbons with a high efficiency. This range of optimal conversion (here defined as the CO–NO crossover point) is also referred to as the 'lambda window' of the catalyst. In the introductory literature, it is frequently assumed that the optimal conversion of all three pollutants occurs at an exactly stoichiometric exhaust composition [1,2]. In practice, it is found that the range of optimal conversion is shifted to slightly fuel-rich exhaust compositions. One purpose of this publication is to investigate the influence of different hydrocarbons on the position of the lambda window.

Current exhaust aftertreatment systems for gasoline vehicles use lambda sensors before and after the catalyst to control the exhaust stoichiometry in such a way that the catalyst remains within its optimal range of operation [3,4]. Since, especially during transient operation, temporary deviations of the exhaust stoichiometry are unavoidable, current three-way catalysts contain ceria as an oxygen-storage compound. The ceria can be partially reduced in a reductive atmosphere and can be reoxidized in an oxidizing atmosphere. The purpose of the lambda control is to maintain the ceria in a partially reduced state so that the catalyst can buffer momentary perturbations of the exhaust composition to the rich and to the lean [5,6]. Today, the storage level of the ceria is determined indirectly with the help of two lambda-probes—one upstream and one downstream of the TWC [7,8].

Recently, novel approaches emerged to detect directly and *in situ* the state of catalysts by measuring the electrical properties of the catalyst coating itself [9]. Two possible principles were considered:

(1) a contact method, for which the coating is applied to planar electrodes and the electrical impedance between these electrodes is measured, and

(2) a non-contact method, in which the coating material is penetrated by radio frequency waves.

The impedance-based method was investigated in detail not only for TWCs [10] but also for Lean NO$_x$ traps (LNT) [11] with good results, but the main disadvantage that prohibits any kind of serial application was the difficulty of contacting the catalysts.

The microwave-based method (also called "microwave cavity perturbation method"), however, that allows for monitoring directly the oxygen loading state of TWCs without any electrical contacts has a higher potential [12,13]. The new method measures the electrical microwave properties (permittivity and conductivity) of the catalyst. In ceria-containing systems, the electrical conductivity of the catalyst strongly depends on the oxidation state of the ceria [14]. Therefore, the method allows for a direct measurement of the filling level of the oxygen buffer. There are two purposes to this study: First, steady-state conversion measurements will be performed to study the influence of different hydrocarbons on the position of the lambda window. It will be shown that the presence of saturated hydrocarbons leads to a shift in position of the optimal conversion window of to fuel-rich compositions. Second, the microwave cavity perturbation method will be used to measure the oxidation state of ceria *in operando* during the conversion measurements. By these in situ experiments, it will be shown that there is a strong correlation between the oxidation state of the ceria and the positions of the lambda window. In addition, it will be shown by titration experiments that a clear correlation exists between the ceria oxidation state and the resonance frequency obtained by the microwave cavity perturbation method.

2. The microwave cavity perturbation technique

The TWC in its steel canning can be considered as a cavity resonator for microwaves [15]. A typical general setup is shown in Fig. 1 (from [13]). The cavity resonator may be coupled to a source and a load via simple "antennas" (e.g. short stubs), which are mounted inside the catalyst canning. Thus, the electrical properties of the catalyst device (ceramic honeycomb plus coating and oxygen storage material) can be measured from the outside.

Electrically, the cavity resonator can be considered as a microwave two-port. If one excites electromagnetic waves with the complex amplitudes a_1 (by one antenna) and a_2 (by the other antenna) and records the complex amplitudes b_1 and b_2 of the backscattered waves by the same antennas, then the wave amplitudes follow Eqs. (1a) and (1b):

$$b_1 = S_{11}a_1 + S_{12}a_2 \quad (1a)$$

$$b_2 = S_{21}a_1 + S_{22}a_2 \quad (1b)$$
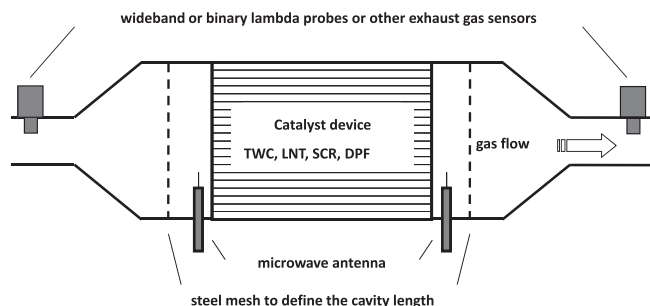
Fig. 1. Scheme of the basic setup of the microwave-based automotive catalyst state diagnosis. The steel meshes are inserted for research purposes only, to exactly define the cavity length. In serial applications they are not required. The wideband lambda probes or other exhaust gas sensors are also for research purposes only. Modified from [13].
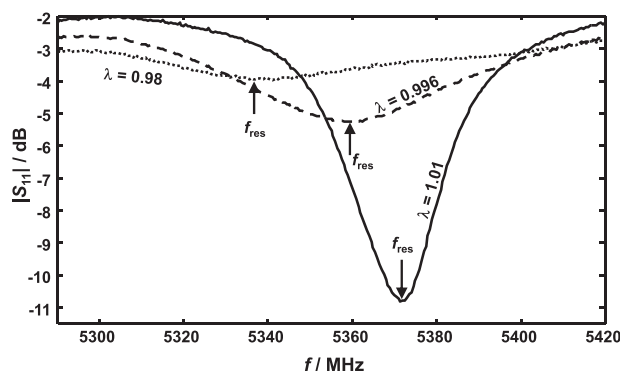
Fig. 2. Example for spectra of the absolute value of the reflection coefficients of a TWC (given in dB). Data: $T = 450\,°C$, GHSV = 65,000 h^{-1}, TWC sample Ø 1″ × 3″ (2.54 cm × 7.62 cm), drawn curve $\lambda = 1.01$, dashed curve $\lambda = 0.996$ and dotted curve $\lambda = 0.98$. See Table 2 with C$_3$H$_8$ for detailed gas compositions. For further experimental details including setup, see [17].

In Eqs. (1a) and (1b), S_{11} is the input reflection coefficient for matched output and S_{22} denotes the output reflection coefficient for matched input. $S_{12} = S_{21}$ are the transmission coefficients, describing the energy transmission from one port to the other. In a laboratory environment, S-parameters are typically measured by vector network analyzers. The squared amplitude of the so-called input reflection coefficient, $S_{11} = b_1/a_1$ for $a_2 = 0$ expresses the power ratio between the reflected and the impinged wave for matched input ($a_2 = 0$). Typically, one finds a behavior as it is shown in Fig. 2 for a completely oxidized, a partially reduced, and a reduced TWC. The minima in the spectra denote resonance modes that occur at distinct resonance frequencies f_{res}. Besides the S_{11} parameters, one may also consider the transmission coefficients [12]. They yield similar results, but require two antennas.

The characteristic resonance spectrum depends on the electrical properties of the TWC (ceramic honeycomb including catalytic coating and oxygen storage material). Since the electronic conductivity of ceria–zirconia solutions depend on their degree of oxidation (from a semiconductor's point of view, the number of Ce^{3+} ions is equivalent with the number of free conduction electrons [16]), a direct catalyst state control determining the overall oxygen loading may be possible by observing the electrical properties of the catalyst.

The resonance frequency of a suitable cavity mode is a direct measure for the amount of stored oxygen. This has initially been shown by careful titrations in both engine dynamometer and laboratory test bench experiments [18,19] and will also be demonstrated below. The physical reason for the resonance frequency shifts are the increasing losses due to Ce^{3+} formation. They broaden the S_{11} curve and shift the resonance frequency [15]. The system is insensitive to other exhaust components like H$_2$, CO$_2$ or CO [20]. However, since the size of the cavity as well as the electrical conductivity of the catalyst materials depends on temperature, temperature effects on the resonance frequency have to be compensated [21]. The early studies have been conducted with Ø 4.66″ × 6″ (11.84 cm × 15.24 cm) full size catalysts, for which the first resonance modes occur at frequencies between 1.2 and 1.5 GHz. Recently, a test setup for small drilled core samples of Ø 1″ × 3″ (2.54 cm × 7.62 cm) has been described [17]. This setup, which has also been used for this work, allows high space velocities and fast temperature ramps.

3. Experimental

A test bench for Ø 1″ × 3″ TWC cores was used in this study to conduct the experiments with a pre-aged TWC (950 °C for 8 h).