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Direct Catalyst Conversion Sensor in Form of a Single Self-Heated Mixed-Potential Device †

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Abstract: Monitoring automotive exhaust gas aftertreatment components is required by law as part of the on-board diagnostics (OBD). For this purpose, a novel sensor device that determines directly the catalyst conversion could be used. It consists of a single, self-heated yttria stabilized ZrO_2-based disc, separating two gas atmospheres. Two identical mixed-potential electrodes yield a voltage signal by comparing a certain trace gas concentration up- and downstream of the catalyst. Measurements in synthetic gas flow verify the theoretical assumption that this voltage signal only depends on the ratio of both concentrations, respectively on the conversion of the catalyst.

Keywords: conversion sensor; on-board diagnostics; mixed-potential sensor; electrochemical comparison; high temperature co-fired ceramics (HTCC)

1. Introduction

To meet present and future limitations of harmful emissions, exhaust gas aftertreatment systems have to be installed in automotive exhaust lines and monitored by on-board diagnostics (OBD) [1–3]. As a possible method to monitor the functionality of a catalyst, a gas sensor could be placed downstream of the catalytic converter, but then only the absolute concentration of a certain analyte gas is known. Therefore, a second sensor has to be placed upstream of the catalyst, allowing determining the conversion by taking into account the signal of the two gas sensors. Of special interest are hydrocarbon sensors, for which many approaches have been reported in literature [4–15]. However, up to now, none of these principles has been serialized. In addition, two different sensors are expensive and they have to have the same functionality, which is difficult to realize, especially with respect to temperature control, sensor ageing, or cross sensitivities. The here-suggested concept consists of only one single device with an output signal that is a monotonous function of the conversion of the catalyst.

2. Sensing Principle

We recently presented a novel sensor device that could be used to measure directly the catalyst conversion by comparing the gas mixtures up- and downstream of a catalyst based on the mixed-potential principle. The sensor consists of a ceramic YSZ disc (YSZ: yttria stabilized zirconium dioxide) with an integrated heater, a reference (RE) and a working (WE) electrode (for details see [16]). An image of the device that is manufactured in high temperature co-fired ceramics (HTCC) can be seen in Figure 1. The heater provides sufficiently high temperatures for ionic conductivity of the solid electrolyte as well as for suitable activity of the electrodes. Furthermore, it is designed to establish a circular temperature distribution in the range of some hundred °C while the rim of the disc is cold enough to apply there low-temperature sealings as for example commonly available plastic O-rings. Then, the device can be assembled in a setup as it is shown in the scheme in Figure 2.

Two bodies for flow control are pressed onto the sensor to provide two hermetically sealed gas compartments that are still connected by the ion conductor.

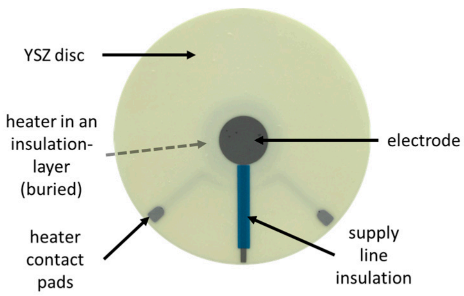

Figure 1. Image of the YSZ sensor disc. The integrated heater meanders around a Pt electrode and is embedded in an insulation layer. It is also buried in the middle of the YSZ disc to provide a homogenous temperature distribution at the electrodes.

The entire sensor device was initially realized as an experimental setup. It looks as shown in Figure 2. The YSZ sensor disc was placed between two PEEK housings so that one electrode (WE) faces a gas atmosphere (half-cell 2) with varying analyte, while the other electrode (RE) is exposed to a reference atmosphere (half-cell 1).

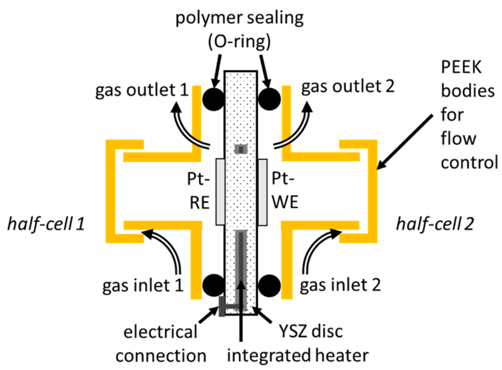

Figure 2. Scheme of the sensor setup to compare electrochemically two gas mixtures.

Now, the YSZ disc acts as a two-sided mixed potential sensor, with a mixed potential of each side that follows the mixed potential theory as explained for instance in [17–19].

Deduced from theory, the sensors voltage signal (U_S) should only depend on catalyst conversion (ξ) even on changing feed gas concentration [20]:

$$\Delta U_S = U_S - U_S(\xi = 0) = const. \cdot \ln(1 - \xi), \quad (1)$$

In Equation (1), the catalyst conversion ξ is defined by the concentrations of the analyte up- and downstream of the catalyst to be monitored (c_{upstream}, $c_{\text{downstream}}$):

$$\xi = (c_{\text{upstream}} - c_{\text{downstream}})/c_{\text{upstream}} \quad (2)$$

In our experimental setup, the gas concentrations in half-cell 1 and half-cell 2 represent the concentrations up- and downstream of the catalyst, respectively. This contribution presents typical mixed-potential measurements in lab atmosphere to verify these considerations. To simulate the behavior of increasing catalyst activity, the content of the analyte (propene) was firstly set constant in both atmospheres, half-cell 1 *and* 2, which is defined as the feed concentration and denotes 0% conversion, i.e., $\xi = 0$. Then, the propene concentration was stepwise reduced in half-cell 2. The ratio between reduced concentration and feed concentration was calculated to a conversion value ξ.

3. Experimental Results

We conducted this experiment three times with different propene feed concentrations in the range of 0 to 100% conversion. The sensor was constantly operated at 500 °C. The sensor signal, which is the measured voltage between both electrodes (U_S), was evaluated at each step. Time dependent raw data show stable values and a fast response. Figure 3 shows the sensor characteristic, i.e., the output voltage U_S as a function of the calculated conversion value ξ. As expected, all measured values are in good agreement to each other and are independent from the propene feed concentration. Note that all values of U_S shown here are not corrected but plotted as measured. Up to 90% propene conversion, the correlation between the theoretical curve and the data is impressing. Especially the fact that the sensor voltage does not depend on the propene concentration of half-cell 1 ($c_{upstream}$) but only on the propene conversion ξ proves our concept. Slight differences occur at higher conversion values (low propene concentrations in half-cell 2, respectively). This effect is under study at the moment.

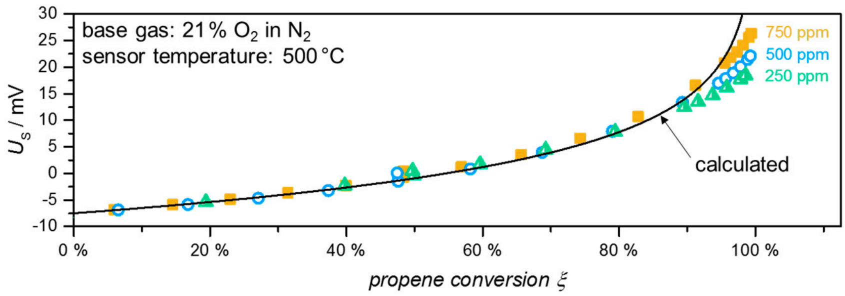

Figure 3. Sensor signal over propene conversion on simulating catalyst behavior for different propene feed concentrations, while the sensor temperature was set to 500 °C. The black curve is calculated from Equation (1) with $U_s(\xi = 0) = 7.5$ mV, for the present sensing principle.

Conflicts of Interest: The authors declare no conflict of interest.

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