**CH₄-Sensitivity of Thermoelectric Gas Sensors**

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**Abstract**

Recently, thermoelectric gas sensors were used for in-situ determination of the CO/HC-content during wood burning. The sensors measure a thermoelectric voltage between a catalytically activated and an inert area. Since the reaction of hydrocarbons takes place exothermically at the catalytic layer, a temperature gradient is generated between the catalyst coating and the inert layer. At an operating temperature of 600°C, a linear relationship can be established between the hydrocarbon concentration and the sensor signal. With methane, however, a huge scattering occurs. Measurements have shown that the oxidation of the highly stable methane molecules at this catalyst just starts at 600°C. The sensitivity of the sensor to methane increases with increasing operating temperature up to 800°C. This information can also be used for a new operating strategy of the sensor.

**Keywords:** thermoelectric gas sensor, exhaust gas sensor, methane sensitivity, hydrocarbon sensor, thermopile

**Introduction**

This paper describes the methane-sensitivity of thermoelectric gas sensors. The thermovoltage between a catalytically activated and an inert area of a special designed thermopile structure is measured. Such sensors are ideal candidates to be used in harsh environments like automotive exhaust or the flue gas of firewood combustion processes [1]. As methane (CH₄) is a climate-damaging pollutant, the need for reliable gas sensing is obvious.

**State of the art**

Recently, thermoelectric gas sensors were successfully applied in the flue gas of firewood combustion. Their signals showed impressive correlation with data from FTIR-analysis during the whole burning process [2]. Such sensors might be applied in future for in-situ determination of the CO/HC-content during wood burning. So, a control algorithm to regulate air streams automatically will help to decrease emissions significantly.

**Description of the sensor setup**

Sensor elements are built up in thick-film technology on alumina substrates (Rubalit 708, CeramTec, Germany). The sensing structure on the front side consists of 15 serial connected thermopiles (made of Pt and PtRh, both from DuPont), meandering between two areas: One area is catalytically coated (we used a porous alumina thick-film with 1 wt.% Pt-loading), the second area is covered inert (QM42, DuPont). A measurable voltage occurs when reducing gases exothermically react at the catalyst and generate a temperature gradient between the catalyst coating and the inert area. To activate the catalyst, the absolute sensor temperature must be controlled to a certain value, which is high enough to exceed the light-off-temperature of the catalyst for most gases. For that purpose, a thick-film heater (made of Pt, LPA-88, Heraeus) was integrated on the reverse side of the substrate (Figure 1). For more details on the sensor setup see Ref. [3].

**Experimental**

To investigate the sensor behavior with respect to methane sensitivity, we conducted lab measurements in synthetic gas atmospheres. In a first experiment, the absolute sensor temperature was kept constant at 600 °C. Methane was admixed in increasing
concentration steps (up to 7000 ppm, base gas: 10 % O₂ in N₂) to provide the sensor characteristic curve. As second experiment, the temperature dependency of the sensor behavior was investigated (base gas: 10 % O₂, 3 % CO₂ and 3 % H₂O in N₂, total flow: 1000 ml/min). With and without test gas (2100 ppm CH₄), the absolute sensor temperature was varied from 150 °C to 800 °C (heating curve) in steps of 25 °C and analogously backwards (cooling curve). The sensor response was calculated as the difference of the sensor signal with and without test gas (Equation 1):

\[ \Delta U_s = U_s(\text{base gas} + CH_4) - U_s(\text{base gas}) \]

**Results and Discussion**

As characteristic curve one expects a linear correlation between test gas concentration and signal change with high reproducibility. We found that for several test gases in former investigations [3]. In the here presented data for CH₄ (Figure 2) a huge scattering is visible.

![Figure 2: Characteristic curve at 600 °C absolute sensor temperature (signal change for several CH₄ concentrations)](image)

This behavior can be explained by the second experiment (Figure 3). Here, it becomes clear that the sensor starts measuring firstly at 600 °C and then its sensitivity strongly increases up to 800 °C. That means, the oxidation of the highly stable methane molecule needs at least 600 °C to be activated at this catalyst. The higher the temperature, the more of the methane reaching the sensors surface is converted and contributes to the sensor response. Slight changes in the catalyst temperature will strongly influence the response.

![Figure 3: Temperature dependent sensor behaviour (signal change upon 2100 ppm CH₄)](image)

One could take these findings as an advantage to discriminate between CH₄ and other gases. Therefore, the operation strategy of the sensor should include measurements at two different temperatures above and below 600 °C and the difference in the response will be attributed to methane in the test atmosphere.

**References**

