Thermoelectric hydrocarbon sensor in thick-film technology for on-board-diagnostics of a diesel oxidation catalyst[☆]

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ABSTRACT

Thermoelectric hydrocarbon sensors were fully manufactured in both alumina substrate-based thick-film technique and low temperature cofired ceramics (LTCC) tape technology. Au–Pt thermocouples were screen-printed on insulating sensor substrates. Porous alumina impregnated with one weight percent platinum was used as catalytic material that covered one side of the sensor. Due to the generated thermal exothermicity, a temperature difference between the catalytically active and the catalytically inactive (reference) side occurred. Additionally, the sensor was equipped with an internal platinum heating element to operate the sensor at temperatures above the light-off temperature of the catalyst material. Owing to the lower thermal conductivity of LTCC, the sensitivity could be improved essentially. To further increase the sensor signal, the number of thermocouples per sensor was enhanced by applying thermopiles of several Au–Pt thermocouples. Therefore, the layout of the heating element was optimized. Altogether, a sensitivity of 0.57 μV/ppm propene was achieved.

1. Introduction

The requirements for exhaust gas aftertreatment of diesel passenger cars have become more stringent in the past few years. In order to reduce CO_2 emissions, leanly operated diesel passenger cars gain market shares. From lean exhausts, nitrogen oxides ($NO_x = NO + NO_2$) cannot be removed by conventional three-way catalysts, e.g. [1]. Therefore, novel exhaust gas aftertreatment concepts are necessary. In ammonia SCR systems (SCR: selective catalytic reduction), urea (in form of a urea water solution) is injected into the exhaust. NH_3 forms in the SCR catalyst and serves as a selective reduction agent for NO_x. The preferred fast SCR reaction requires an oxidation of NO to NO_2 – preferably in equimolar portions to enhance the low temperature activity [2,3]. Therefore, diesel oxidation catalysts (DOCs) are installed to convert NO partly to NO_2. To reduce hydrocarbon cold start emissions, close-coupled DOCs with low thermal masses are installed. These platinum-based catalysts oxidize CO and unburnt hydrocarbons (C_xH_y) to carbon dioxide (CO_2) and water (H_2O). Very highly dispersed platinum,

which is stabilized against thermal sintering, is applied to meet the required performance and durability [4]. Such DOCs reach their light-off temperature very rapidly to abate hydrocarbon cold-start emissions. If the DOC is located in front of the diesel particulate filter (DPF), the converted NO_2 promotes the low temperature soot oxidation [5]. In the case of additionally injected hydrocarbons, the C_xH_y conversion increases the exhaust gas temperature [6] to initiate the burn-off of trapped soot. Thus, the DOC is an emission relevant component, which has to be monitored in the context of on-board diagnostics (OBD) [7]. The occurrence of unburnt hydrocarbons downstream of a diesel oxidation catalyst is a hint for its malfunction [8]. Therefore, hydrocarbon sensors may be appropriate for future on-board diagnostics.

While in literature a couple of principles to detect hydrocarbons are described [9–12], only a few papers are dealing with applications of such sensors in the harsh automotive exhaust. Also the thermoelectric or calorimetric sensing principle is described in the literature to detect inflammable gases like CO, CH_4, H_2 or C_xH_y in gaseous samples or for the use in medical examinations [13–16] but not in the harsh automotive exhaust. One of the few studies that are dealing with a calorimetric hydrocarbon sensor for automotive applications utilizing a high Seebeck coefficient is Ref. [17].

For such sensors, a thermoelectric hydrocarbon sensor that bases on the reaction enthalpy of the unburnt hydrocarbons is investigated. The sensors measure the resulting temperature

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difference between a catalytically active and a catalytically inactive part of a sensor. Therefore at least one thermocouple (connection of two conducting materials) has to be applied on a sensor substrate to detect the temperature difference. To further improve this technology we used also substrate materials with a much lower thermal conductivity, as suggested in [17]. Additionally, a heating element on the rear side of the sensor allows operating the sensor above the light-off temperature of the catalytically material.

2. Experimental and modeling

2.1. Sensor setup

The also-called indirect thermoelectric sensor [18] was fully manufactured in thick-film and ceramic tape technology. Two conducting materials, here gold and platinum, were applied on the substrate to form a thermocouple. As substrate materials alumina (*CeramTec*, 96%) was used for one embodiment of the sensor and LTCC tape (*DuPont*, 951) for an advanced second version. One junction of the two metals Au and Pt was covered with a catalytically inactive layer, whereas the other one was coated with a highly catalytically active layer. Fig. 1a shows a sketch of the sensor side of such a sensor device. Owing to the temperature increase at the catalytic layer due to the oxidation of hydrocarbons, a thermovoltage (U_{th}) between the two junctions occurs acc. to Eq. (1).

$$U_{th} = k_{AB} \cdot (T_{cat,hot} - T_{inactive}) \qquad (1)$$

Herein, $T_{cat,hot}$ denotes the temperature over the catalyst-covered film, and $T_{inactive}$ is the temperature of the inactively covered side. The Seebeck coefficient between Au and Pt is given by k_{AB}. It depends on temperature. Data are taken from [19]. Due to the lower thermal conductivity of the LTCC material, a higher temperature difference between the hot and the cold sensor side is expected. Hence, a higher sensor sensitivity is expected. Furthermore, as shown in Fig. 1b, the thermovoltage can be increased by applying several thermocouples and connecting them

in series ("thermopile principle", see e.g. [20,21]). Thus, the resulting thermoelectric voltages are multiplied by the number n of thermocouples according to Eq. (2). In this study, we used sensors with $n = 1$, 3, and 9 thermocouple on alumina substrates as well as sensors on LTCC substrates. For the latter, we varied the sensor layout once more, so that $n = 15$ thermocouples could have been attached.

$$U_{th} = n \cdot k_{AB} \cdot (T_{cat,hot} - T_{inactive}) \qquad (2)$$

2.2. Preparation of the catalytic material

The catalyst coating was prepared by impregnating porous Al_2O_3 powder (Baikowski CR10, BET specific surface area: $7\,m^2/g$, crystal Structure: 95%α, 5%γ, agglomerate size d_{90}: 1.25 μm) with platinum in the form of the platinum complex [$(NH_3)_4Pt]Cl_2 \cdot H_2O$ (Sigma–Aldrich). A defined amount of the platinum complex was dissolved in deionized water. The carrier ceramic alumina was mixed into the solution, with a mass ratio of 100:1 ($m_{Al_2O_3}$: $m_{Pt\,complex}$). Due to the previous solution process of the metal complex, a more homogeneous distribution of Pt in the alumina is expected using this procedure [22,23]. After drying the solution at 120 °C, the powder was reduced, to bring Pt in the metallic, catalytically active state acc. to the following reactions:

$$Pt^{2+} + 2e^- \rightarrow PtO$$

$$H_2 + 2Cl^- \rightarrow 2HCl + 2e^-$$

$$[Pt]Cl_2 + H_2 \rightarrow 2HCl + [Pt]^0$$
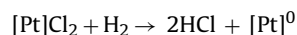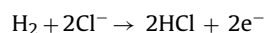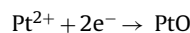
The powders were reduced in a vertical reactor at 500 °C for 1 h under forming gas (5% H_2 in N_2). A screen-printable paste of the catalytic material was prepared by mixing the sieved powder (<90 μm) with a thixotropic organic binder (terpineol, ethyl cellulose).
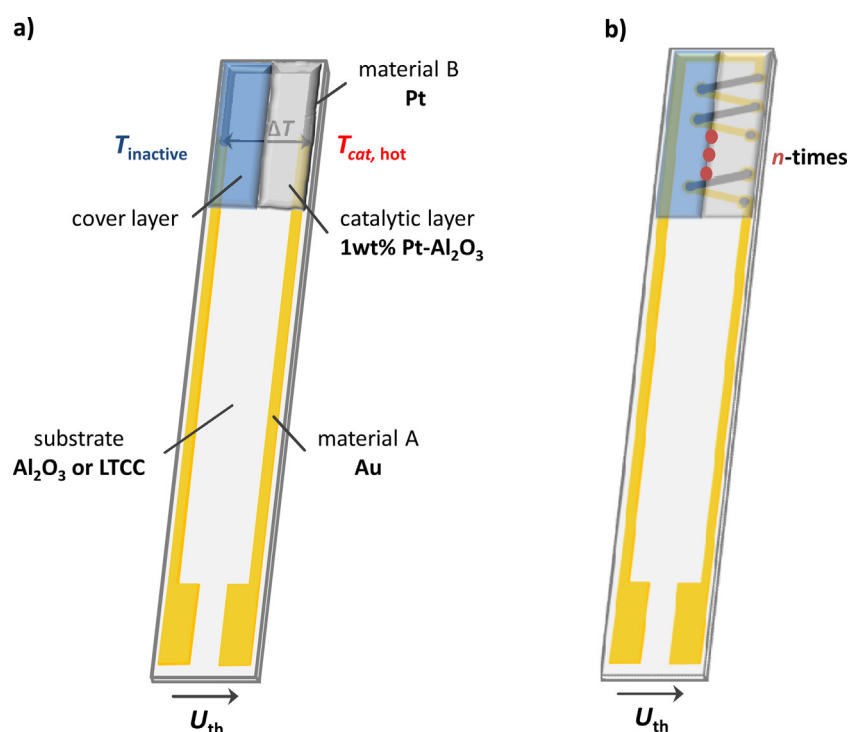

Fig. 1. Scheme of the thermoelectric sensors (sensor side): (a) sensor with one thermocouple; (b) sensor with multiple thermocouples.