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Examination of New Catalysts for Catalytic Combustible Gas Sensors by Thermal Analysis

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Summary:
DTA was used to investigate cobalt oxide (Co_3O_4) catalysts, which differ essentially in terms of particle morphology, to their thermal response towards methane (CH_4) oxidation in dry air. Moreover, the thermal stability and the effect of hydrogen sulfide (H_2S) inhibitor on the thermal behavior of the Co_3O_4 catalyst was examined by DTA. A comparison of the DTA measurement with a MEMS pellistor based on a modified Co_3O_4 catalyst shows a similar behaviour of their responses to CH_4 and H_2S. The obtained results demonstrate the reliability of the method for preselection of catalysts for their application in catalytic gas sensors.

Keywords: metal oxide catalysts, catalytic gas sensor, poisons, Differential Thermal Analysis (DTA).

Background, Motivation and Objective

In the field of safety technology, catalytic sensors, so-called »pellistors«, are commonly used for detection of flammable gases such as hydrocarbons. The heat produced during catalytic oxidation of the combustible gas on the catalytic layer corresponds to its concentration in environment. Currently, pellistors usually operate at high temperatures (>450°C) to ensure the proper detection of methane, which is the most inert combustible gas.

The high operation temperatures as well as the presence of catalyst inhibitors like hydrogen sulfide (H_2S) and sulfur dioxide (SO_2) or poisons like silicones lead in turn to a high power consumption, short or long-term deactivation of catalyst and thus a shortened sensor life. Novel catalysts are required to lower the operating temperature and extend the service life. However, the development of new catalysts for the targeted gas sensor applications turns out to be difficult due to various factors influencing the sensor response, which are not easy to differentiate [1].

To overcome the limitations, existing by investigations of pellistor gas sensors, Differential Thermal Analysis (DTA) [2] can be used for preselection and investigation of possible catalyst materials [1]. The thermal response of a catalyst powder induced through oxidation of target gas can be measured and used for direct comparison of different catalysts.

Here, we demonstrate DTA investigations on the impact of particle size and morphology of Co_3O_4 catalysts on their thermal response to CH_4 oxidation and the thermal stability as well as the effect of H_2S exposure. The pellistor response of Co_3O_4 related catalyst deposited on MEMS-based hotplate sensor [3] to CH_4 and H_2S is shown for comparison. The focus of the examinations was on lower operation temperatures (<400°C). Spinel Co_3O_4 is used for investigations due to its promising catalytic properties for CH_4 combustion [4].

Description of the New Method

The commercially available DTA device (NETZSCH, STA 409) was adapted for the investigation of catalyst´s gas reaction at dry conditions. The DTA signal is measured as voltage signal normalized to sample weight (µV/mg) and correlates with the temperature difference between empty reference and sample crucible resulted from a heat release or heat uptake. If heat is released (exothermic oxidation reaction) the DTA signal shows a negative output.

Results

In order to investigate the impact of particle size and morphology on the thermal response, wet

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grinded commercial Co_3O_4 with spherical nanoparticles and Co_3O_4 synthesized by precipitation exhibiting nanoparticles of random shape were used for investigations. Fig. 1 illustrates the DTA response of commercial Co_3O_4 in comparison to the synthesized one to the exposure of 1 vol. % CH_4 for 30 min at different temperatures. While the commercial Co_3O_4 shows a pronounced activity firstly at 450°C, the synthetized Co_3O_4 with particles of random shape exhibits already at 350°C a considerable response. For both catalysts, the thermal stabilty test (synthetic air/methane alternation at 350°C and 450°C) were undertaken. The synthetisized Co_3O_4 exhibits a slighly lower thermal stability than commercial one originated from operation at high temperatures (450°C).

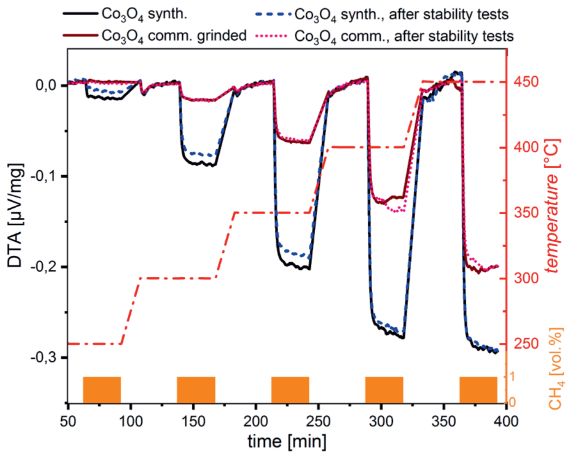

Fig. 1. DTA response to the exposure of 1 vol.% CH_4 in dry air for 30 min at temperatures between 250-450°C for two different Co_3O_4 catalysts before and after thermal stability investigations.

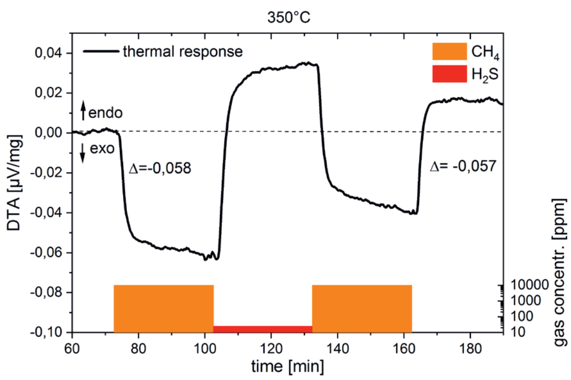

Fig. 2. DTA response of commercial Co_3O_4 catalyst to the exposure of 1 vol.% CH_4 and 25 ppm H_2S in dry air for 30 min each at 350°C. A purge with synthetic dry air for 30 min was used to achieve a base line.

Furthermore, the effect of H_2S exposure on thermal response of commercial Co_3O_4 catalyst to methane was examined (Fig. 2). In particular, when H_2S is introduced into the chamber after methane, the positive output is observed, which indicates the endothermic reaction taking place on the catalyst. When CH_4 is introduced directly after H_2S, the same signal output as before H_2S exposure is obtained with some baseline drift evidencing that short H_2S exposition times have no effect on the catalytic reaction. The same thermal behavior towards CH_4 and H_2S was observed by testing of Co_3O_4 related catalyst in pellistor (Fig. 3), with exception of the baseline shift. In pellistor measurements, the positive output corresponds to the exothermic oxidation of CH_4.

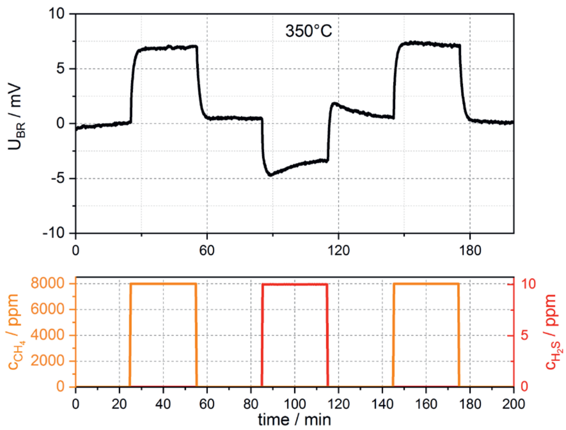

Fig. 3. Pellistor sensor output to 8000 ppm CH_4 and 10 ppm H_2S in dry air at 350°C for Co_3O_4 related catalyst.

The obtained results illustrate the applicability of DTA measurements for previous testing of catalysts offering many opportunities for further investigations.

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