DOI 10.5162/SMSI2020/P1.4

Systematic Investigations on the Reaction Potential of Catalytic Sensor Materials

Olena Yurchenko[1,2], Hans-Fridtjof Pernau[1], Laura Engel[1], Benedikt Bierer[1], Martin Jägle[1], Jürgen Wöllenstein[1,2]

[1]Fraunhofer Institute for Physical Measurement Techniques IPM, Heidenhofstr. 8, 79110 Freiburg, Germany,
[2]Department of Microsystems Engineering—IMTEK, University of Freiburg, Georges-Koehler-Allee 102, 79110 Freiburg, Germany
olena.yurchenko@ipm.fraunhofer.de

Summary:
We present Simultaneous Thermal Analysis (STA) as a systematic approach for investigation of catalytic activity at ideal conditions and for thermal stability. The investigations were performed on different cobalt oxide samples differing in particle size, which is a promising catalyst for methane oxidation. 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 activity, catalytic gas sensor, Simultaneous Thermal Analysis (STA), catalyst preselection.

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. The nowadays pellistors usually operates at high temperatures (>450°C) to ensure the proper detection of methane which is the most inert combustible gas.

However, the high operation temperatures entail some disadvantages such as high power consumption and lowered catalyst stability. Reducing the operating temperature will contribute to decrease the power consumption and increases of sensor operating life due to improving of catalyst aging. To reduce the operation temperature, catalysts of high activity and stability are required, especially for detection of methane.

However, the choice of suitable catalysts for the targeted gas sensor applications is not easy from different points of view. Firstly, catalysts used in sensors are complex systems consisting of catalysts and various additives allowing their integration into the sensor and generates the mechanical stability of the layer. Additives can affect the catalyst activity as well as stability and their effect is difficult to identify by gas sensor characterization. Secondly, the response detected by a sensor is the complex reaction as well, determined by the whole sensor system. Thirdly, the preparation process of individual sensors is quite extensive. That additionally limits the amount of tested catalyst samples and the variation of parameters.

To overcome these limitations, existing by investigations of pellistor gas sensors, different calorimetric methods can be used to perform the preselection of the catalysts [1, 2]. The usage of additional gas analyzing systems makes the calorimetric investigations more reliable. We used Simultaneous Thermogravimetry-Differential Thermal Analysis System coupled with Quadrupole Mass Spectrometer (STA-QMS) to investigate systematically the effect of particle size distribution and morphology of Co_3O_4 on its catalytic activity for methane oxidation and its thermal stability. The focus of investigation was on lower operation temperatures (<400°C). Spinel Co_3O_4 was reported as a promising catalyst for methane combustion [3]. The investigations aim at the ascertainment of Co_3O_4 applicability as catalyst or as support of metallic catalyst in pellistors achieving low operation temperatures.

Description of the New Method

The commercially available STA (NETZSCH, STA 409 CD-QMS 403/5 SKIMMER) was adapted for the investigation of catalytic activity at dry conditions. The temperature difference between reference and sample crucible (contained ≈20 mg sample) was converted by software in DTA signal (µV/mg) corresponding to catalytic activity. Due to the heat release during catalytic oxidation, the DTA signal shows a negative output. The signal normalization to sample weight allows systematic investigations and direct comparison between different samples.

Results

To investigate the effect of particle size distribution on catalytic activity, commercial Co_3O_4 (400 mesh, 37 µm) was wet grinded in a zircon jar by means of a planetary ball mill for different durations (between 0.5h and 16h). Additionally, Co_3O_4 was synthesized by precipitating procedure obtaining nanosized particles.

Fig. 1 illustrates the dependence of DTA response of commercial Co_3O_4 on the grinding time at different temperatures. The increasing the grinding time leads to successive improving the catalytic activity, especially for the first four hour of grinding. Further increasing the grinding time has no significant effect on improving the catalytic activity.

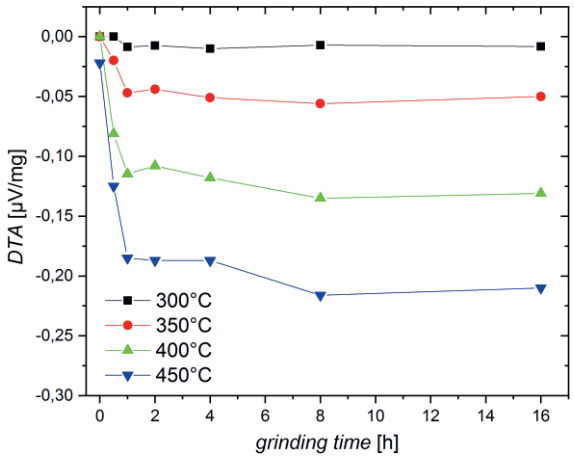

Fig. 1. DTA response as a measure of catalytic activity obtained at CH_4 oxidation (1 vol.% in dry air) on commercial Co_3O_4 catalysts as a function of grinding time and operation temperature.

Fig. 2 shows that for this catalyst, a pronounced activity is observed at 450°C. In contrast, the synthetized Co_3O_4 with initially nanosized particles shows already at 350°C a considerably higher activity. For both kinds of catalyst, the thermic stabilty test (synthetic air/methane alternation at 350°C and 450°C) were undertaken (Fig. 3). As expected, synthetisized nanosized Co_3O_4 exhibits slighly lower thermal stability than commercial one originated from operation at high temperatures (450°C).

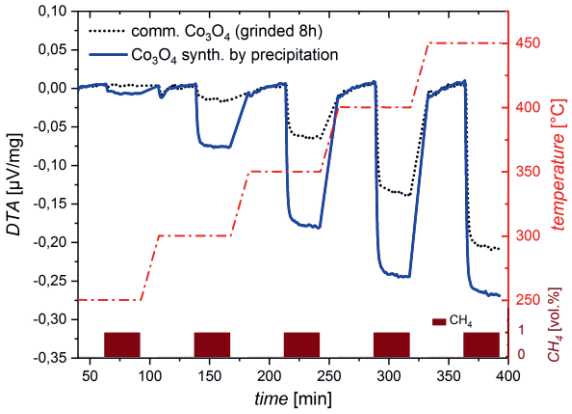

Fig. 2. DTA response to the exposure of 1 vol.% CH_4 in dry air for 30 min at temperatures between 250-450°C for two different Co_3O_4 catalysts; a rinsing with synthetic dry air for 30 min was used to achieve a base line.

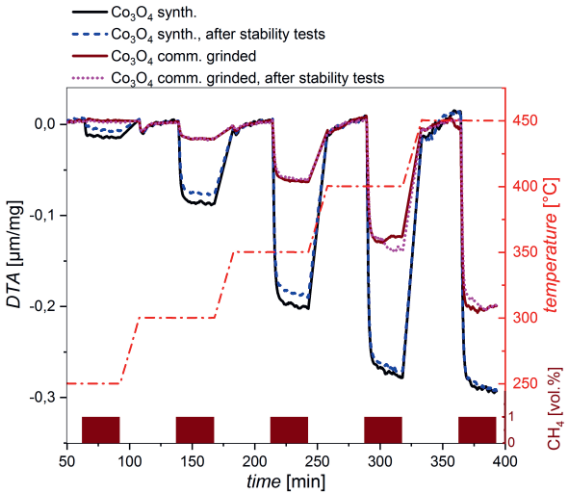

Fig. 3. DTA response to the exposure of 1 vol.% CH_4 in dry air for 30 min at temperatures between 250-450°C for two different Co_3O_4 catalysts before and after thermal stability investigations.

References

[1] J.Loskyll, W.F.Maier, K.Stoewe, Application of a Simultaneous TGA-DSC Thermal Analysis System for High-Throughput Screening of Catalytic Activity. *ACS Comb. Sci.* 14, 600−604 (2012); doi:10.1021/co3000659.

[2] G. Hakvoort, X. Xiaoding, Decompostion of methanol vapour over solid catalyst, measured by DSC. *J. Thermal Anal.* 37, 1269-1279 (1991); doi:10.1007/BF01913860

[3] Z. Pu, H. Zhou, Y. Zheng, W. Huang, X. Li, Enhanced methane combustion over Co_3O_4 catalysts prepared by a facile precipitation method: Effect of aging time. Appl. Surf. Sci. 410, 14-21 (2017); doi:10.1016/j.apsusc.2017.02.186.