

Impact of cobalt oxide morphology on the thermal response to methane examined by thermal analysis

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Summary:

In the present talk, we will demonstrate the impact of particle size and morphology of a metal oxide catalyst on its catalytic ability towards methane oxidation examined in a wide temperature range at dry environmental conditions. The investigations were performed by differential thermal analysis (DTA) technique delivering the thermal response of different cobalt oxide samples differing in particle size. The obtained results demonstrate the reliability of the method for preselection of catalysts for their application in catalytic gas sensors by the example of cobalt oxide, which is a promising catalyst for methane oxidation.

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

Background, Motivation and Objective

Catalytic gas sensors, so-called “pellistors”, are commonly used for detection of combustible gases in order to warn the formation of potentially explosive atmospheres. In pellistors, combustible gases are detected by the heat produced through their catalytic oxidation on the active sensor coated with a catalytic layer. To initiate the catalytic oxidation of gases on the catalyst, the sensor is held at a specific operation temperature. The currently pellistors usually operate 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 a decrease in power consumption and an increase of the sensor's operating life due to the decelerated catalyst aging. For the reduction of the operation temperature, catalysts of high activity and stability are required, especially for detection of methane.

Pd or Pt particles finely dispersed on aluminum oxide is the most common choice of catalyst material for pellistors [1]. However, recent ad-

vances in catalytic combustion evidences that some metal oxides could have certain advantages over aluminum oxide based catalysts. Thereby, the particle size and morphology of catalytic material have a determining effect on its catalytic behavior.

In this context, we investigated systematically the effect of particle size distribution and morphology of Co₃O₄ catalysts on their catalytic activity to methane oxidation and their thermal stability. The focus of investigation was on lower operation temperatures (<400°C). Spinel Co₃O₄ was reported as a promising catalyst for methane combustion [2]. Differential Thermal Analysis (DTA) was used as investigation method that provides a voltage signal in case of an oxidation reaction of the test gas on catalyst surface [3]. Two different methods were applied to produce Co₃O₄ catalysts with different particle size and morphology, a grinding of micro-sized particles and a direct synthesis.

The investigations aim at the ascertainment of Co₃O₄ applicability as catalyst or as support of metallic catalyst in pellistors that achieve low operation temperatures.

Description of the New Method

The commercially available STA (NETZSCH, STA 409 CD-QMS 403/5 SKIMMER) equipped with a DTA sample carrier was adapted for the investigation of catalytic activity at dry environmental conditions. Thereby, the temperature difference between the sample and reference crucible is measured as a voltage at defined environmental temperature (isothermal conditions) and gas atmosphere. The temperature difference between reference and sample crucible (contained ≈ 20 mg sample) was converted by software in a DTA signal ($\mu\text{V}/\text{mg}$) corresponding to the catalytic activity. Due to the heat release during the catalytic oxidation, the DTA signal shows a negative output. The signal normalization on the sample weight allows systematic investigation and direct comparison between different samples.

To investigate the effect of particle size distribution on catalytic activity, commercial Co_3O_4 (400 mesh, $37\ \mu\text{m}$) 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.

Results

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

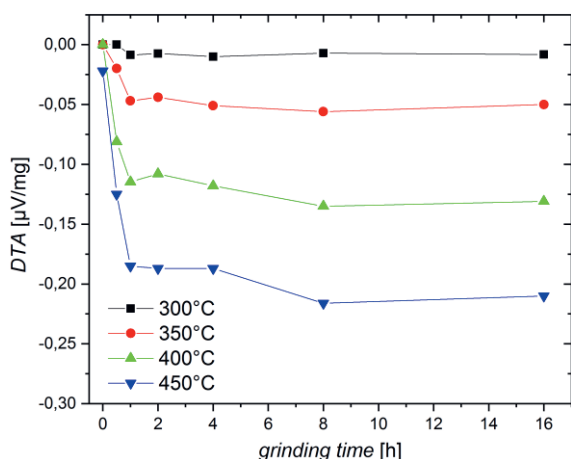


Fig. 1. DTA response as a measure of catalytic activity obtained at CH_4 oxidation (1 vol.% in dry air) on commercial Co_3O_4 catalysts as a function of grinding time and operation temperature.

Fig. 2 shows the thermal response of commercial catalyst grinded for 8h in comparison to response of synthesized Co_3O_4 . It is visible that for the grinded catalyst, a

pronounced activity is observed at 400°C and 450°C . In contrast, the synthesized Co_3O_4 with initially nanosized particles already shows a significantly higher activity at 350°C .

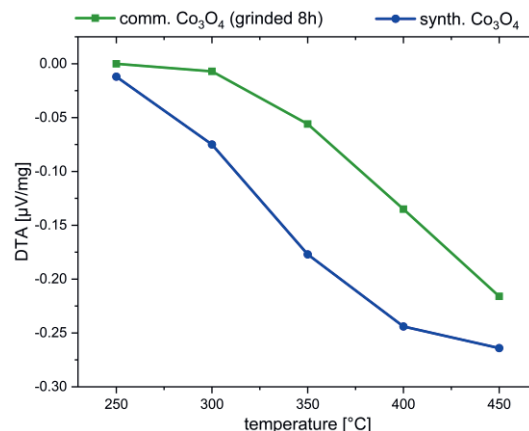


Fig. 2. DTA response obtained at CH_4 oxidation (1 vol.% in dry air) on commercial Co_3O_4 catalyst grinded for 8h and synthesized Co_3O_4 catalyst at different operation temperatures.

For both kinds of catalyst, thermal stability tests (synthetic air/methane alternation at 350°C and 450°C) were undertaken. The results indicate that synthesized nanosized Co_3O_4 exhibits a slightly lower thermal stability than the commercial one originated by operation at high temperatures (450°C).

References

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