proceedings

MDPI

Abstract

Co_3O_4-Based Materials as Catalysts for Catalytic Gas Sensors †

Olena Yurchenko [1,*], Patrick Diehle [2], Katrin Schmitt [1,3] and Jürgen Wöllenstein [1,3]

[1] Fraunhofer Institute for Physical Measurement Techniques (IPM), 79110 Freiburg, Germany; katrin.schmitt@ipm.fraunhofer.de (K.S.); juergen.woellenstein@ipm.fraunhofer.de (J.W.)
[2] Fraunhofer Institute for Microstructure of Materials and Systems (IMWS), 06120 Halle, Germany; patrick.diehle@imws.fraunhofer.de
[3] Department of Microsystems Engineering (IMTEK), University of Freiburg, 79110 Freiburg, Germany
* Correspondence: olena.yurchenko@ipm.fraunhofer.de
† Presented at the XXXV EUROSENSORS Conference, Lecce, Italy, 10–13 September 2023.

Abstract: The work deals with the development of Co_3O_4-based catalysts for application in catalytic gas sensors. Among the transition-metal oxide catalysts, cobalt oxide exhibits the highest activity in catalytic combustion. The catalytic activity of the catalysts was examined by Differential Scanning Calorimetry (DSC), evaluating the catalyst's activity by measuring its thermal response to 1% methane (CH_4).

Keywords: cobalt oxide; catalyst; catalytic sensors; morphology

1. Introduction

Catalytic gas sensors are widely used to detect flammable gases to safely monitor the lower explosive limit (LEL). They were first described by Alan Baker in the early 1960s. Alumina-based catalysts with a high amount of Pd and Pt are used to ensure the proper detection of gases, especially of CH_4, for a required lifetime mainly due to the strong tendency of Pd-based catalysts to deactivate throughout operation. In view of the scarcity of precious metals, these catalysts should be substituted through metal-oxide catalysts containing none or only a low loading of noble metals.

Spinel-type Co_3O_4 is active for the catalytic combustion of CH_4 due its structure with variable valence states (Co^{2+}/Co^{3+}) [1]. Moreover, the doping of Co_3O_4 with further transition metals like Cr, Mn, Cu or Ni should improve further its catalytic ability. Especially the mixed Co_3O_4-based spinel $NiCo_2O_4$ with a Ni:Co molar ratio of 1:2 has been reported to have excellent catalytic properties towards CH_4 oxidation [2]. However, it was demonstrated by several studies that the morphology of Co_3O_4 plays a decisive role in catalytic activity due to variations in the crystal structure, formation of surface defects and surface-active species [3].

In the present work we investigated and analyzed the influence of the morphology and doping of Co_3O_4 with Ni on its catalytic activity using the DSC method which measures thermal response.

2. Materials and Methods

Pure (mCo_3O_4 and sCo_3O_4) and Ni-doped Co_3O_4 ($NiCo_2O_4$, $Ni_{0.5}Co_{2.5}O_4$) catalysts were synthesized by the same precipitating procedure as described in [2]. The difference between mCo_3O_4 and sCo_3O_4 catalysts is the atmosphere used during synthesis (N_2 or air).

Scanning transmission electron microscope (STEM) equipped with a secondary electron detector (SE) (Hitachi, Japan) was used to visualize the morphology of the catalysts. Differential Scanning Calorimetry (DSC, Netzsch, Selb, Germany) was used to examine thermal response of the catalysts to 1% CH_4 [4].

check for updates

Citation: Yurchenko, O.; Diehle, P.; Schmitt, K.; Wöllenstein, J. Co_3O_4-Based Materials as Catalysts for Catalytic Gas Sensors. *Proceedings* **2024**, *97*, 21. https://doi.org/10.3390/proceedings2024097021

Academic Editors: Pietro Siciliano and Luca Francioso

Published: 14 March 2024

3. Discussion

In Figure 1 the different morphologies of the investigated Co_3O_4 catalysts are demonstrated.

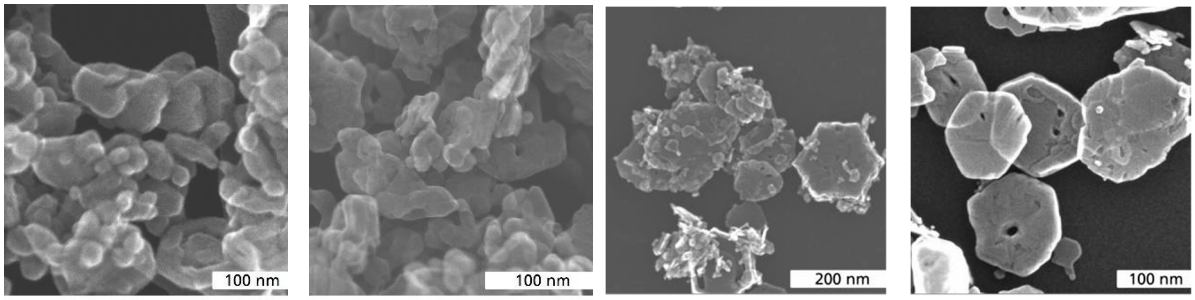

Figure 1. SE-STEM images of (**a**) mCo_3O_4; (**b**) sCo_3O_4; (**c**) $NiCo_2O_4$; (**d**) $Ni_{0.5}Co_{2.5}O_4$ metal-oxides.

Figure 2 shows the corresponding thermal responses at temperatures between 250 and 450 °C.

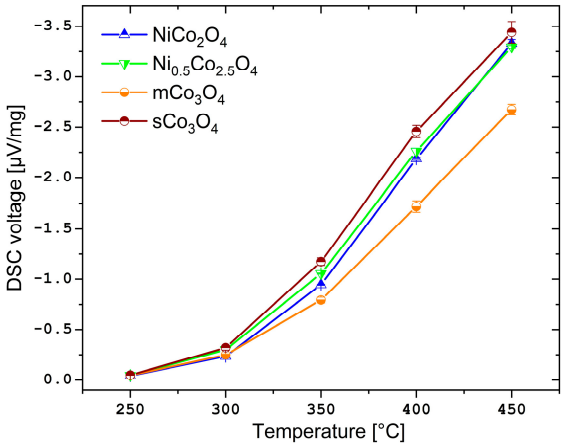

Figure 2. Temperature dependent DSC response of four investigated catalysts to 1% CH_4.

sCo_3O_4 reveals a significantly higher thermal response than the two Ni doped oxides and mCo_3O_4. The reason for this is the different morphology and the structure of the metal oxide. In our study, the effect of the catalyst morphology on their activity and thermal stability will be analyzed and discussed in detail.

Author Contributions: Conceptualization, O.Y.; methodology, O.Y. and P.D.; investigation, O.Y. and P.D.; writing—original draft preparation, O.Y.; writing—review and editing, O.Y., P.D., K.S. and J.W.; supervision, J.W. and K.S.; funding acquisition, J.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Fraunhofer Gesellschaft within the FluMEMS project and the Federal Ministry of Education and Research within European funding program Eurostars in project MEscal E! 113779 as well as within the project HySABi (03EN5009C).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Dataset available on request from the authors.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Zheng, Y.; Yu, Y.; Zhou, H.; Huang, W.; Pu, Z. Combustion of lean methane over Co_3O_4 catalysts prepared with different cobalt precursors. *RSC Adv.* **2020**, *10*, 4490–4498. [CrossRef] [PubMed]
2. Tao, F.F.; Shan, J.-J.; Nguyen, L.; Wang, Z.; Zhang, S.; Zhang, L.; Wu, Z.; Huang, W.; Zeng, S.; Hu, P. Understanding complete oxidation of methane on spinel oxides at a molecular level. *Nat. Commun.* **2015**, *65*, 7798. [CrossRef] [PubMed]
3. Datye, A.K.; Votsmeier, M. Opportunities and challenges in the development of advanced materials for emission control catalysts. *Nat. Mater.* **2020**, *20*, 1049–1059. [CrossRef] [PubMed]
4. Yurchenko, O.; Pernau, H.-F.; Engel, L.; Bierer, B.; Jägle, M.; Wöllenstein, J. Impact of particle size and morphology of cobalt oxide on the thermal response to methane examined by thermal analysis. *J. Sens. Sens. Syst.* **2021**, *10*, 37–42. [CrossRef]