

Article

Accelerated Deactivation of Mesoporous Co_3O_4 -Supported Au–Pd Catalyst through Gas Sensor Operation

Xuemeng Lyu ^{1,2} , Olena Yurchenko ², Patrick Diehle ³, Frank Altmann ³, Jürgen Wöllenstein ^{1,2} and Katrin Schmitt ^{1,2,*} 

¹ Department of Microsystems Engineering (IMTEK), University of Freiburg, 79110 Freiburg, Germany; xuemeng.lyu@ipm.fraunhofer.de (X.L.); juergen.woellenstein@ipm.fraunhofer.de (J.W.)

² Fraunhofer Institute for Physical Measurement Techniques (IPM), 79110 Freiburg, Germany; olena.yurchenko@ipm.fraunhofer.de

³ Fraunhofer Institute for Microstructure of Materials and Systems (IMWS), 06120 Halle, Germany; patrick.diehle@imws.fraunhofer.de (P.D.); frank.altmann@imws.fraunhofer.de (F.A.)

* Correspondence: katrin.schmitt@ipm.fraunhofer.de; Tel.: +49-203-67583

Abstract: High activity of a catalyst and its thermal stability over a lifetime are essential for catalytic applications, including catalytic gas sensors. Highly porous materials are attractive to support metal catalysts because they can carry a large quantity of well-dispersed metal nanoparticles, which are well-accessible for reactants. The present work investigates the long-term stability of mesoporous Co_3O_4 -supported Au–Pd catalyst (Au–Pd@meso- Co_3O_4), with a metal loading of 7.5 wt% and catalytically active mesoporous Co_3O_4 (meso- Co_3O_4) for use in catalytic gas sensors. Both catalysts were characterized concerning their sensor response towards different concentrations of methane and propane (0.05–1%) at operating temperatures ranging from 200 °C to 400 °C for a duration of 400 h. The initially high sensor response of Au–Pd@meso- Co_3O_4 to methane and propane decreased significantly after a long-term operation, while the sensor response of meso- Co_3O_4 without metallic catalyst was less affected. Electron microscopy studies revealed that the hollow mesoporous structure of the Co_3O_4 support is lost in the presence of Au–Pd particles. Additionally, Ostwald ripening of Au–Pd nanoparticles was observed. The morphology of pure meso- Co_3O_4 was less altered. The low thermodynamical stability of mesoporous structure and low phase transformation temperature of Co_3O_4 , as well as high metal loading, are parameters influencing the accelerated sintering and deactivation of Au–Pd@meso- Co_3O_4 catalyst. Despite its high catalytic activity, Au–Pd@meso- Co_3O_4 is not long-term stable at increased operating temperatures and is thus not well-suited for gas sensors.

Keywords: catalytic gas sensor; pellistor; methane; propane; catalyst deactivation; mesoporous Co_3O_4 , Au–Pd nanoparticles



Citation: Lyu, X.; Yurchenko, O.; Diehle, P.; Altmann, F.; Wöllenstein, J.; Schmitt, K. Accelerated Deactivation of Mesoporous Co_3O_4 -Supported Au–Pd Catalyst through Gas Sensor Operation. *Chemosensors* **2023**, *11*, 271. <https://doi.org/10.3390/chemosensors11050271>

Academic Editor: Jianxin Yi

Received: 7 March 2023

Revised: 25 April 2023

Accepted: 27 April 2023

Published: 2 May 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Catalysts which are able to catalyze combustion reactions at lower operation temperatures (≤ 400 °C) are of great interest for different application areas, e.g., for volatile organic compound (VOC) removal or abatement of methane emissions from coal mines [1–4]. Particularly, the oxidation of highly stable methane (CH_4) molecules requires catalysts with high activity and/or high operation temperatures [4]. Supported palladium (Pd) is the most active catalyst for methane combustion. Indeed, the structure of the Pd catalyst, e.g., the ratio between metallic Pd^0 and PdO_x phases, is essential for its catalytic performance at given reaction conditions [5,6]. It was repeatedly reported that the catalytic performance of Pd catalysts could be improved through Pd alloying with Au for different catalytic reactions [7–10], including methane combustion [9,11–13]. Au, as an alloying component, could have a positive effect on the regulation of the active phase of Pd particles or act as an electronic promoter for Pd [7,10,14].

The support also plays an important role in the control of the catalyst structure. Among different metal oxides, spinel-type Co_3O_4 is an interesting compound as a support for noble metals. Its structure with variable valence states ($\text{Co}^{2+}/\text{Co}^{3+}$) makes it also active for the catalytic combustion of methane [15]. Furthermore, the strong interaction between Co_3O_4 and Pd^{2+} in $\text{Pd}/\text{Co}_3\text{O}_4$ catalysts is supposed to enhance the catalyst activity for methane combustion [16].

An increase in the surface area and the optimization of the morphology of the support materials, including Co_3O_4 , has attracted increased attention in recent times. Thus, it was demonstrated by several studies that the morphology of Co_3O_4 plays an important role in catalyst activity [16]. The support materials with high surface area and porosity offer an advantage for metal-supported catalysts in terms of improved dispersion of metallic particles. Metal loading on the support is the decisive factor for the reaction temperature [16,17]. A higher metal loading allows a lowering of the reaction temperature for the effective oxidation of methane. However, the loss of specific activity is typically observed for higher metal loading due to the metal particle agglomeration and reduced dispersion [16,18]. Nevertheless, catalysts with high Pd loadings are currently applied to ensure the proper oxidation of methane [19] for a required lifetime [20], mainly due to the strong tendency of Pd-based catalysts to deactivate throughout the operation.

Three-dimensional ordered, mesoporous metal oxides are the focus of interest as support material through the design of customized catalysts because the reactants have a sufficiently accessible high surface area, and the metal particles are stable in a dispersed state [11–13,21].

In this context, we examined in previous works mesoporous Co_3O_4 -supported Au–Pd nanoparticles ($\text{Au-Pd@meso-Co}_3\text{O}_4$) as catalysts for application in catalytic combustion sensors [22,23]. Catalytic combustion sensors are essential devices for the early detection of flammable and explosive gases in various applications, e.g., in coal mines, petroleum drilling, landfills and domestic fields [24,25]. Among other target gases, the main components of natural gas, methane and propane, are typical for detection with catalytic combustion sensors [26]. One of the most common catalytic combustion sensors is the so-called pellistor. The sensing principle is based on the detection of heat generated by the oxidation of the target gas on the catalyst deposited on the sensor substrate [27]. For pellistors, catalysts of high activity to methane oxidation are required to give a satisfying output signal, reduce power consumption and avoid thermal aging effects [25,28,29]. The $\text{Au-Pd@meso-Co}_3\text{O}_4$ catalyst, composed of three-dimensional ordered mesoporous Co_3O_4 synthesized by a template method, and alloyed Au–Pd nanoparticles prepared by colloidal synthesis according to Zhixing [11], achieved a favorable gas sensing performance towards methane and propane at low operating temperatures of 400 °C [23]. The improved gas sensing characteristics of the catalyst were attributed to the ordered mesoporous Co_3O_4 with a large specific surface area, enabling a high load with uniformly dispersed Au–Pd nanoparticles up to 7.5 wt% according to energy-dispersive X-ray (EDX) analysis.

The catalyst stability over the sensor lifetime is an important issue with respect to the application. Especially the catalytic combustion sensor, as a safety device, must be satisfactory in terms of catalyst long-term stability, which mainly defines sensor reliability and lifetime. The catalyst deactivation under operation temperatures is one aspect of catalyst stability. The previous works of other authors on related metal-supported mesoporous oxide catalysts, e.g., $1.93\text{AuPd}/\text{meso-CoCr}_2\text{O}_4$ [12], $2.9\text{AuPd}/\text{meso-Co}_3\text{O}_4$ and $0.6\text{Pt}/\text{meso-Co}_3\text{O}_4$ [11,30], reported no significant thermal stability problems for catalysts in methane combustion investigated on a short time scale (between 24 h and 60 h on-stream). Nevertheless, there are studies reporting a loss of performance of porous metal oxide catalysts by thermal treatment, e.g., Chen, et al. [31], described the deactivation of hierarchically structured NiCo_2O_4 spinel oxide observed after catalyst treatment at 500 °C for 2 h indicating the catalyst susceptibility to increased temperatures. The reason for deactivation was the destruction of the catalyst microstructure because of the thermal treatment.

Therefore, the focus of our investigations was the examination of the stability of Au–Pd@meso-Co₃O₄ catalyst on long-time scales (624 h) under operating conditions of the pellistor. The Au–Pd@meso-Co₃O₄ catalyst with high metal loading of 7.5 wt% was characterized concerning its sensor response towards different concentrations of methane and propane in a temperature range from 200 °C to 400 °C. The measurements were repeated to compare the sensor response of the fresh and used catalysts. The identical measurements were also performed using a meso-Co₃O₄ catalyst without metal loading to investigate the effect of Au–Pd particles on catalyst aging. The morphological aging of the catalysts was examined using a scanning transmission electron microscope (STEM) equipped with a secondary electron detector to visualize the surface topography with a lateral resolution of approximately 1 nm.

2. Materials and Methods

2.1. Materials

The synthesis process of mesoporous Co₃O₄ supported alloyed Au–Pd nanoparticles (Au–Pd@meso-Co₃O₄) was introduced in our former work [22,23]. The synthesis was performed according to Zhixing, et al. [11]. Shortly, mesoporous Co₃O₄ (meso-Co₃O₄) was synthesized by mixing Co(NO₃)₂·6H₂O (2 g, 10.9 mmol, Sigma-Aldrich, St. Louis, MO, USA, purity ≥ 98%) in toluene (50 mL) with self-synthesized KIT-6 template (1 g) which was used as a structured frame directing the metal oxide growth [32]. After being stirred for 3 h, the solid mixture was filtered and calcined at 600 °C for 4 h in the air to decompose the nitrate salt and to form Co₃O₄ according to the structure of the template. Next, hot NaOH (2 mol L^{−1}) was applied at 70 °C to remove the silica template. Subsequently, the product was washed with DI water twice and then with ethanol twice. After overnight drying in an oven at 80 °C, the mesoporous Co₃O₄ was obtained. XRD measurements confirmed the crystalline structure of the meso-Co₃O₄ material [22].

Colloidal synthesis was used to prepare alloying Au–Pd nanoparticles with narrow particle size distribution. Au–Pd particles were prepared as follows: gold (III) chloride trihydrate (Sigma-Aldrich, purity ≥ 99.9%) and palladium (II) chloride (Sigma-Aldrich, ReagentPlus, 99%) was mixed in DI water in an ice bath. The molar ratio of Au: Pd was 1:2. A certain amount of surface stabilizer polyvinyl alcohol (PVA, Sigma-Aldrich, Mw 9000–10,000, 80% hydrolyzed) was added into noble metal salt aqueous solution to ensure that the mass ratio between noble metal and PVA is 1:1.5. Then, 0.1 mol L^{−1} of the reducing agent sodium borohydride (Sigma-Aldrich, purum p.a., ≥96%) was added into the reactor rapidly to keep the molar ratio between noble metal and NaBH₄ 1.5:1. A dark brown solution containing Au–Pd particles was formed immediately.

For preparation of the Au–Pd@meso-Co₃O₄ catalyst, a desired amount of mesoporous Co₃O₄ was mixed with Au–Pd alloy solution and stirred for 12 h. After filtration with deionized (DI) water, the Au–Pd@PVA@meso-Co₃O₄ material was calcined at 400 °C for 6 h to remove the polymer surface stabilizer and to anchor the particles on the metal oxide surface. Finally, an Au–Pd@meso-Co₃O₄ catalyst loaded with 7.5 wt% of Au–Pd particles was obtained, as confirmed by EDX analysis [22].

2.2. Sensor Preparation for Gas Characterization

Ceramic micro-substrates with a size of 2.3 × 2.1 × 0.4 mm³ (IST AG, Ebnet-Kappel, Switzerland) were used to set up a pellistor sensor. The substrates contain a platinum heater which functions simultaneously as a temperature-sensing element. The advantage of the used substrate is its robustness and the linear temperature coefficient of resistance (TCR) for platinum. A pellistor sensor is made up of two substrates. The first one without any coating acts as a non-active reference substrate, while the second one with catalyst coating is the active sensor component responding to combustible gases. Pellistors measure the thermal response of the catalyst produced by catalytic oxidation of target gases. The thermal reaction of the catalyst is detected by measuring the output voltage from a Wheatstone Bridge, arising from the temperature difference between both substrates. The thermal response

corresponds directly to the concentration of oxidized gas in the environment [29,33]. The experiments were carried out with both catalysts, meso-Co₃O₄ and Au-Pd@meso-Co₃O₄. To deposit the catalyst on the active sensor substrate, both materials were dispersed in DI water with a solid content of 15 g L⁻¹. Then, the prepared dispersions were deposited on the substrates with a micropipette. After deposition, the coated substrates were heated in dry air at 400 °C for 12 h to stabilize the catalyst layer on the substrate. Finally, the coated substrates were welded onto TO39 sockets for gas characterizations.

2.3. Gas Sensitive Characterization

Four equal sets of experiments were performed on meso-Co₃O₄ and Au-Pd@meso-Co₃O₄ catalysts integrated into one sensor device. One set was composed of the measurement series carried out sequentially for different gas concentrations and at several operating temperatures (400 °C, 350 °C, 300 °C, 250 °C and 200 °C) firstly for methane and then for propane. Methane is a representative compound for hardly oxidizing gases, while propane is an easily oxidizing, flammable gas. The gas concentrations of methane and propane were 1%, 0.75%, 0.5%, 0.3%, 0.1%, 0.07% and 0.05%. The important concentration ranges for pellistor applications are between 1% and 0.3% or 0.1% for detection of methane and propane, respectively.

All gas measurements were carried out in a closed gas chamber filled consecutively with synthetic air (21% O₂, 79% N₂; Westfalen AG, Münster, Germany) and with the target gas of the specified concentration; each measurement period lasted 1 h. To obtain the defined target gas concentration, the gases (10.00 vol% CH₄ or 10.00 vol% C₃H₈ in synthetic air; Westfalen, Germany) were mixed with synthetic air as a gas carrier using calibrated mass flow controllers (Vögtlin Instruments, Muttenz, Switzerland). The measurements from the first set were referred to as the fresh catalyst measurements, and from the fourth set as the measurements on the used catalyst. The overall duration of all experiments for each catalyst was 624 h.

2.4. Electron Microscopy Investigations

The surface topography of the catalyst was investigated by a probe-corrected transmission electron microscope (Hitachi HF 5000) equipped with an in-lens secondary electron (SE) detector and operated at 200 kV. The microscope was operated in scanning transmission electron microscopy mode, and the corresponding SE signal was recorded, which will be referred to as SE-STEM.

SE-STEM investigations were performed on freshly synthesized Au-Pd@meso-Co₃O₄ catalyst and on Au-Pd@meso-Co₃O₄ catalyst after gas experiments to examine morphological changes of the catalyst. To investigate the role of Au-Pd nanoparticles on the stability of Au-Pd@meso-Co₃O₄ as an entire catalytic system, the investigations were also performed on the pure meso-Co₃O₄ catalyst as a reference system after conducting gas experiments.

To directly investigate the surface of the catalyst on the sensor substrate without any alteration by the sample preparation, bulk-like samples with a thickness larger than 500 µm were prepared by a special sample preparation procedure. This procedure includes removal of contact wires, fixing the sample (sensor substrate with catalyst) on a copper ring which acts as sample support and the removal of protruding parts of the sensor substrate as well as the reduction of its thickness by laser. The applied sample preparation ensures that the sample surface is not influenced.

3. Results and Discussion

3.1. Characterization of Gas Sensors

A series of experiments with different concentrations of methane and propane was carried out in a temperature range from 200 °C to 400 °C to investigate the long-term stability of Au-Pd@meso-Co₃O₄ and meso-Co₃O₄ catalysts under operation conditions of a pellistor. It has to be taken into account that the given temperature reflects the temperature at the substrate and not at the surface of the catalyst. The temperature of the catalyst

depends on the heat of the reaction. The more catalytic active Au-Pd@meso-Co₃O₄ catalyst experienced a much higher temperature than the meso-Co₃O₄ catalyst.

In Figure 1, the gas sensor signal as the output voltage of fresh Au-Pd@meso-Co₃O₄ catalyst to different concentrations of (a) methane, and (b) propane at 400 °C is shown in comparison to the signal of the used catalyst. When comparing the output voltages of Figure 1a with that of Figure 1b, it is visible that the oxidation of propane induces a considerably higher sensor signal than methane of the same concentration, e.g., five times higher for 1% gas concentration. The reasons for that are the higher standard reaction enthalpy for propane oxidation (2220 kJ/mol) compared to methane oxidation (890 kJ/mol) and the higher reactivity of propane for catalytic oxidation as well [34]. Moreover, Figure 1 reveals a remarkable decrease in the sensor signal for the used Au-Pd@meso-Co₃O₄ catalyst for both gases, although the baseline maintains stability.

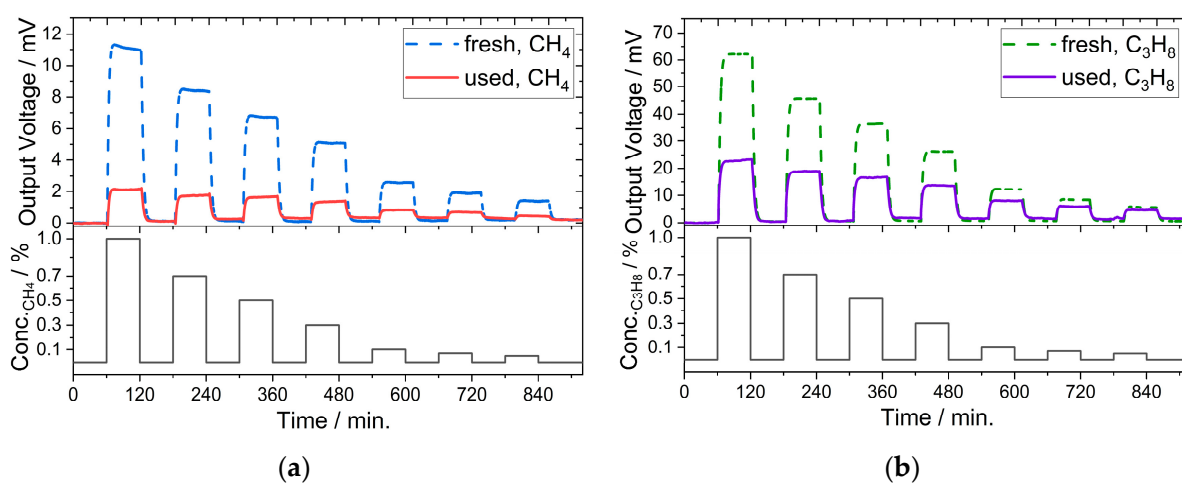


Figure 1. Concentration-dependent gas sensor signal of Au-Pd@meso-Co₃O₄ catalyst measured at 400 °C for fresh and used catalyst towards (a) methane, and (b) propane gas mixture in dry synthetic air.

The signal of the fresh pellistor decreases rapidly with increasing methane concentration, while the signal of the used one is almost linear with methane concentration. This indicates a significant decrease in the number of active sites where catalytic reactions can occur. Whereas the reduction in catalytic capacity is greatly reduced in the early stages of the long-term stability test, i.e., for the fresh pellistor, the sintering and aging of the mesoporous structure and the aggregation of Au-Pd are rapid. When the material has degraded to a certain degree, the system reaches an energy minimum, i.e., the stabilization point, after which the collapse of the mesoporous structure and the aggregation of the alloy becomes more difficult. Thus, the signal of the used pellistor is proportional to the concentration.

For propane (Figure 1b), on the other hand, we have observed that both show almost a linear relationship. A possible explanation is that the formation process of reactants becomes more complicated for propane due to the increase of its carbon chain. The formation of these intermediates and the covering of the catalyst surface by continued oxidation becomes, to some extent, a protection against the rapid collapse of the mesoporous material. At the same time, the mesoporous material under propane combustion reaches a steady state very quickly with the help of thermodynamics, as the exothermic heat of propane combustion is much higher than that of methane, resulting in a fresh material that exhibits the same linearity as the used material.

To simplify the data representation, Figure 2 illustrates the average gas sensor response of fresh and used Au-Pd@meso-Co₃O₄ catalyst to various concentrations of both gases as well as the concentration-dependent residual response measured at 400 °C. The residual response (in %) was calculated from the relation between the average gas sensor response

of the used and fresh catalyst. The pellistor demonstrates an almost linear concentration dependency of average gas sensor response for fresh Au-Pd@meso-Co₃O₄ catalyst to methane (Figure 2a) and propane (Figure 2b) in a concentration range between 0.1 and 1%. The linearity of the concentration dependency is maintained for both gases after a long-term operation, although an unexpectedly high decrease in the sensor sensitivity is observed, indicating considerable aging of the catalyst. The output voltage is decreased from 11.1 mV to 2.2 mV for 1% of methane and from 61.6 mV to 22.9 mV for 1% of propane, demonstrating that the sensitivity of the sensor to methane is more impaired than to propane due to higher signal drop. This evidences that the reaction sites of high activity, which are necessary for methane oxidation, are more affected by the aging process than the sites of moderate activity sufficient for propane oxidation [24,35]. That is confirmed by an examination of the residual response (Figure 2c). For increased methane concentration, the residual response of Au-Pd@meso-Co₃O₄ remains unchanged at the same low value of 20%. In the propane measurement, as the concentration increases, the residual response reduces from 56% for 0.1% C₃H₈ to 37% for 1% C₃H₈, indicating that the oxidation of high propane concentrations becomes less effective on the used catalyst. Such an oxidation behavior of the Au-Pd@meso-Co₃O₄ catalyst could be explained by a strongly decreased concentration of highly active sites needed for methane oxidation in the process of catalyst aging. The moderately active sites are less influenced; however, their activity is not enough for the effective oxidation of high propane concentrations.

Next, the mesoporous Co₃O₄ support was investigated under the same operating conditions to gain more insight into the role of the support and nanoparticles on the catalytic performance of Au-Pd@meso-Co₃O₄ catalyst. Figure 3 illustrates the pellistor average gas sensor response of meso-Co₃O₄ catalyst, in a fresh and used state, to various concentrations of methane (Figure 3a) and propane (Figure 3b) along with calculated residual response at 400 °C (Figure 3c). As expected, the average gas sensor response of meso-Co₃O₄ is significantly lower than that of Au-Pd@meso-Co₃O₄ at all concentrations of methane and propane (e.g., up to 8 times for methane and up to 17 times for propane) indicating the substantial contribution of alloyed Au-Pd particles to the overall catalytic activity of the catalyst. Moreover, Au-Pd@meso-Co₃O₄ has a higher activation effect for propane than meso-Co₃O₄. The sensor signal of fresh Au-Pd@meso-Co₃O₄ and meso-Co₃O₄ to 1% C₃H₈ are 5.5 times or 2.7 times higher than 1% CH₄ (compare Figure 2a,b and Figure 3a,b), respectively. It is noteworthy that the catalytic activity of meso-Co₃O₄ underwent a significant decline during sensor operation as well. However, unlike Au-Pd@meso-Co₃O₄, meso-Co₃O₄ shows a higher decrease in activity to propane compared to methane. Output voltage drops for 1% C₃H₈ from 3.57 mV to 1.13 mV compared with 1.34 mV to 0.92 mV for 1% CH₄.

Additional information is given by residual response (Figure 3c). As the methane concentration increases, the residual response of meso-Co₃O₄ rises from 26% to 70%, suggesting that the conversion of methane on the remaining reaction sites becomes more effective with higher gas concentrations. The residual response of meso-Co₃O₄ to different concentrations of propane is at approximately the same low level of 35%. A reasonable explanation is that highly active sites of meso-Co₃O₄ needed for CH₄ oxidation are less affected by catalyst aging than the sites in Au-Pd@meso-Co₃O₄. The higher residual response of meso-Co₃O₄ at higher methane concentration results from a more effective methane activation on the aged catalyst when more molecules are available for adsorption. Since the catalytic activation of methane is impeded due to a limited ability to bind to the catalytic surface [19]. In the case of propane, the activity of meso-Co₃O₄ was from the beginning low and is more affected by aging. The reason is due to the complex oxidation process of propane which includes more intermediate steps until the molecule gets totally oxidized [36,37]. It seems that the oxidation of the propane molecule is not complete on meso-Co₃O₄.

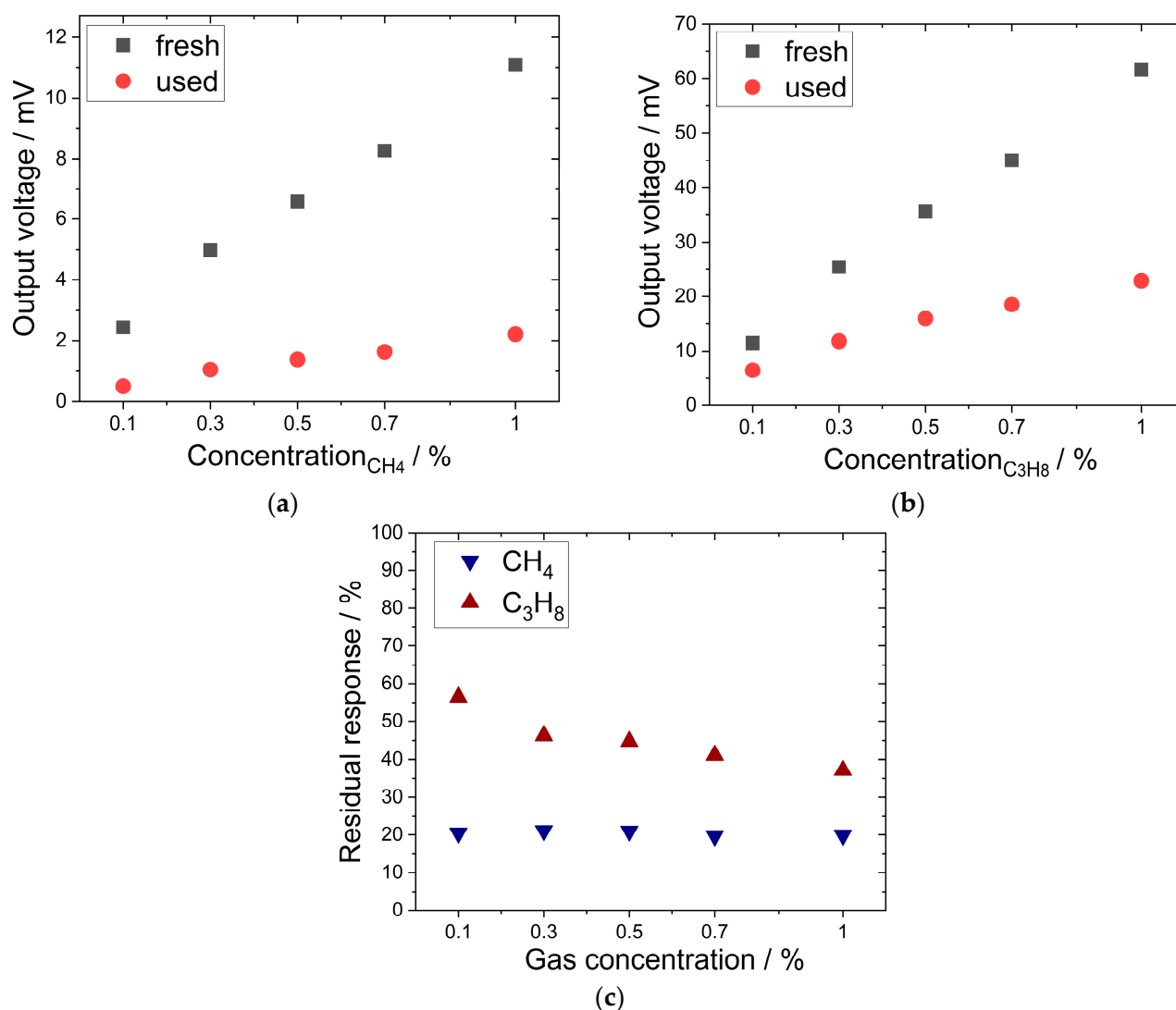


Figure 2. Concentration-dependent pellistor average response of Au-Pd@meso-Co₃O₄ for fresh (black) and used material (red) to (a) methane, and (b) propane at 400 °C. Residual response of Au-Pd@meso-Co₃O₄ (c) to methane and propane at gas concentrations of 0.1%, 0.3%, 0.5%, 0.7% and 1%.

Figure 4 provides results of residual responses of Au-Pd@meso-Co₃O₄ (a) and meso-Co₃O₄ (b) catalysts to methane and propane obtained at four operation temperatures.

Figure 4a,b imply that the residual response of both materials depends only scarcely on the operation temperature. The slight response fluctuation could partially be caused by the measurement uncertainty and continued aging of the catalysts. The residual response of Au-Pd@meso-Co₃O₄ to methane and propane is similar at all temperatures and is in the range between 20% and 38%. The meso-Co₃O₄ exhibits an unusually high residual response to methane in the range between 70% and 85% but a low residual response to propane in the range between 20% and 35%.

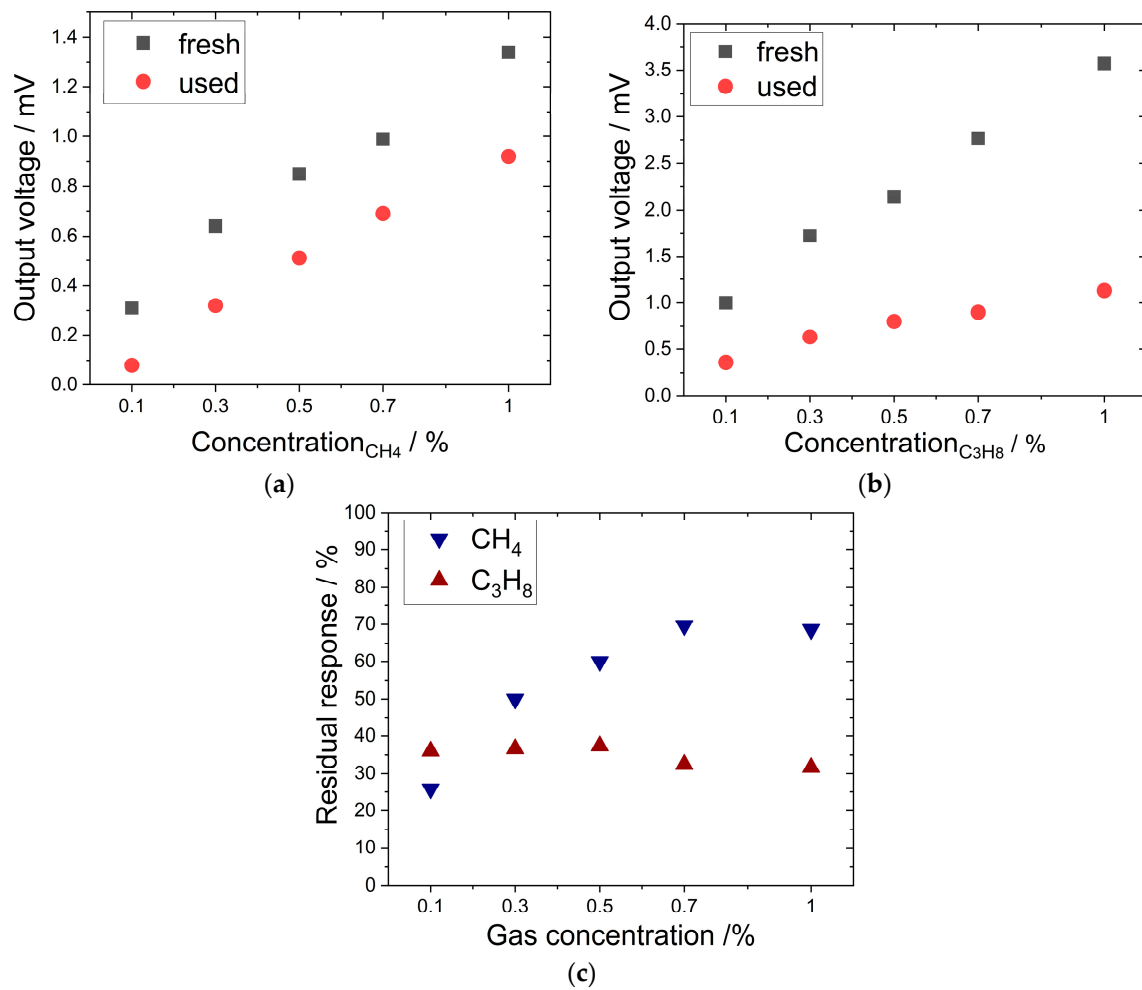


Figure 3. Concentration-dependent pellistor average response of meso-Co₃O₄ for fresh (black) and used material (red) to (a) methane, and (b) propane at 400 °C. Concentration-dependent residual response of meso-Co₃O₄ (c) to methane and propane. Methane and propane concentrations were 0.1%, 0.3%, 0.5%, 0.7% and 1%.

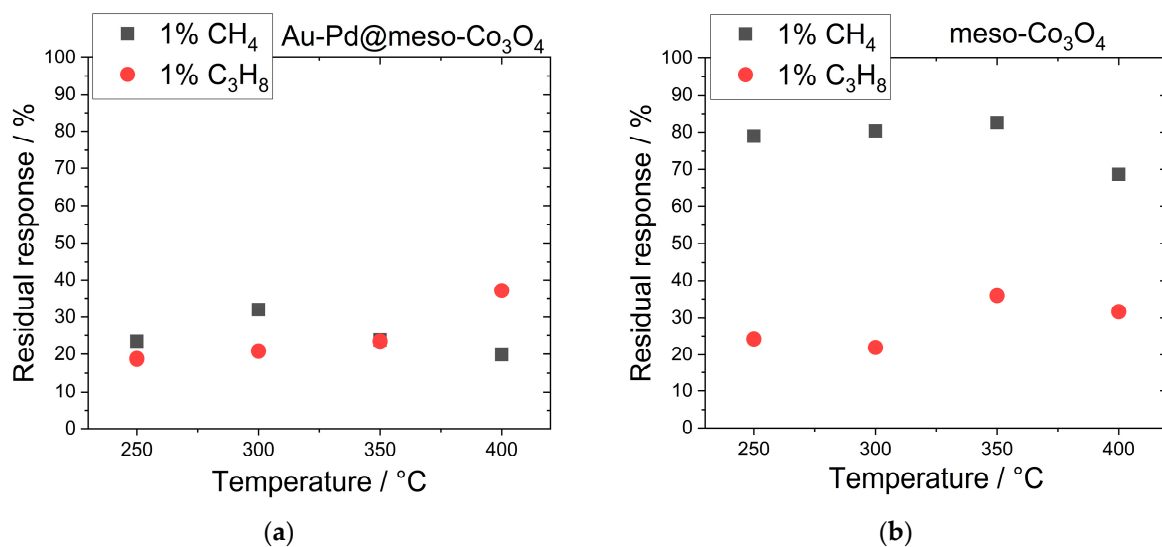


Figure 4. Residual response of (a) Au-Pd@meso-Co₃O₄, and (b) meso-Co₃O₄ catalysts under various operating temperatures to 1 vol% methane and propane.

3.2. Morphological Characterization

The performed gas experiments revealed that the catalytic response is considerably reduced for both kinds of catalyst systems (Au–Pd@meso- Co_3O_4 and meso- Co_3O_4) during continuous gas measurements, which indicates degradation of the catalyst. Since we did not perform any tests with catalyst inhibitors, the catalyst deactivation due to chemical poisoning was not expected [38,39]. The decreasing number of active sites is often accompanied by a reduction of the active surface area and changes in morphology due to thermal aging typically occurring at higher temperatures. Therefore, the surface morphology of the catalyst system was investigated by SE-STEM. The Au–Pd@meso- Co_3O_4 catalyst was investigated directly after synthesis and after 624 h of operation at varied concentrations of methane and propane and at different temperatures, while the meso- Co_3O_4 catalyst was only investigated after performing gas measurements.

Figure 5 shows the original morphology of the Au–Pd@meso- Co_3O_4 catalyst. It could be noticed that the freshly synthesized material has a loose three-dimensional frame structure, and the mesopores are evenly dispersed, building a well-defined symmetric hollow network. The noble alloy nanoparticles seen as spheres are evenly distributed over the surface. Moreover, Au–Pd nanoparticles are also observed inside the surface near pores. In combination with previous investigations in transmission, we conclude that the AuPd-nanoparticles are homogeneously dispersed throughout the complete mesoporous network [22,23]. Thus, the mesoporous system of Co_3O_4 provides a high specific surface area for anchoring nanoparticles and a high number of active sites for catalytic reactions, which explains the high activity of the catalyst. The average particle size of Au–Pd alloyed nanoparticles was determined to be 5.6 nm with a size distribution between 4 and 8 nm.

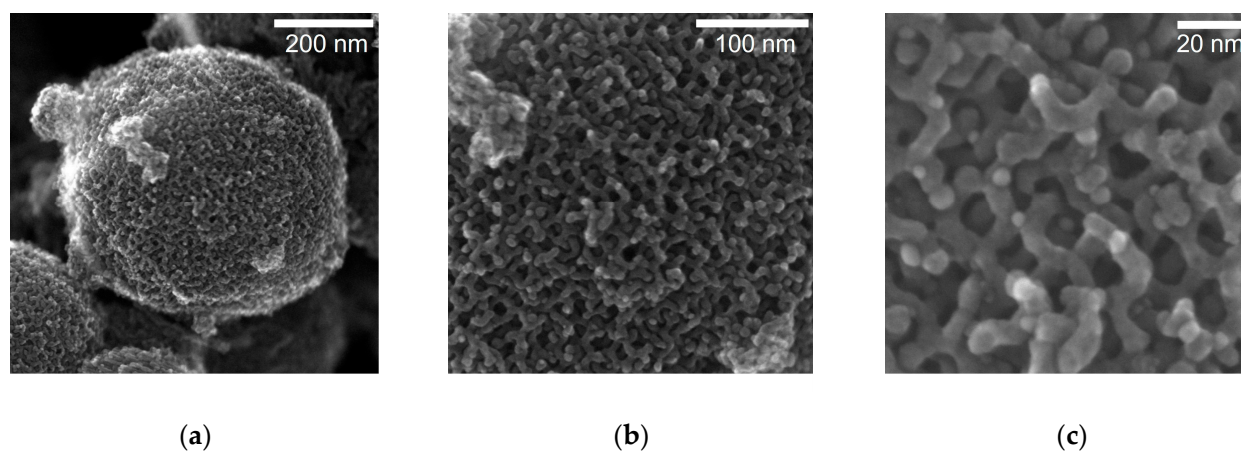


Figure 5. SE-STEM images of freshly synthesized Au–Pd@meso- Co_3O_4 at different magnifications of the same ROI. (a) complete three-dimensional frame structure at low magnification (b) at higher magnification, the evenly distributed mesopores are visible (c) the high magnification shows the Au–Pd nanoparticles in the mesopores.

Figure 6a–c show the same material after the long-term operation of the sensor. In comparison to the fresh catalyst, the images of the aged Au–Pd@meso- Co_3O_4 sample surface reveal two effects implying sintering. Firstly, the mesoporous structure of Co_3O_4 support has collapsed at the surface, accompanied by shrinking and partial or complete closure of mesopores. In some places, even the formation of completely closed surfaces through advanced sintering was visible (Figure 6c). Thus, the porous network inside the mesoporous structure of Co_3O_4 is less accessible by the gas, leading to a reduction of the specific surface area. The second observation is the significant enlargement of Au–Pd particles, which are of spherical shape with an average diameter of 11.5 nm. Simultaneously, significantly smaller particles of 1–3 nm, as indicated by arrows, coexist with notably larger particles. The increase in particle size means the reduction of the specific surface area of the metal catalyst. Furthermore, the particles are situated preferably inside the shrunken pores,

which is an energetically stable position for nanoparticles [40]. Therefore, the particles inside the porous network are less accessible to gases [41].

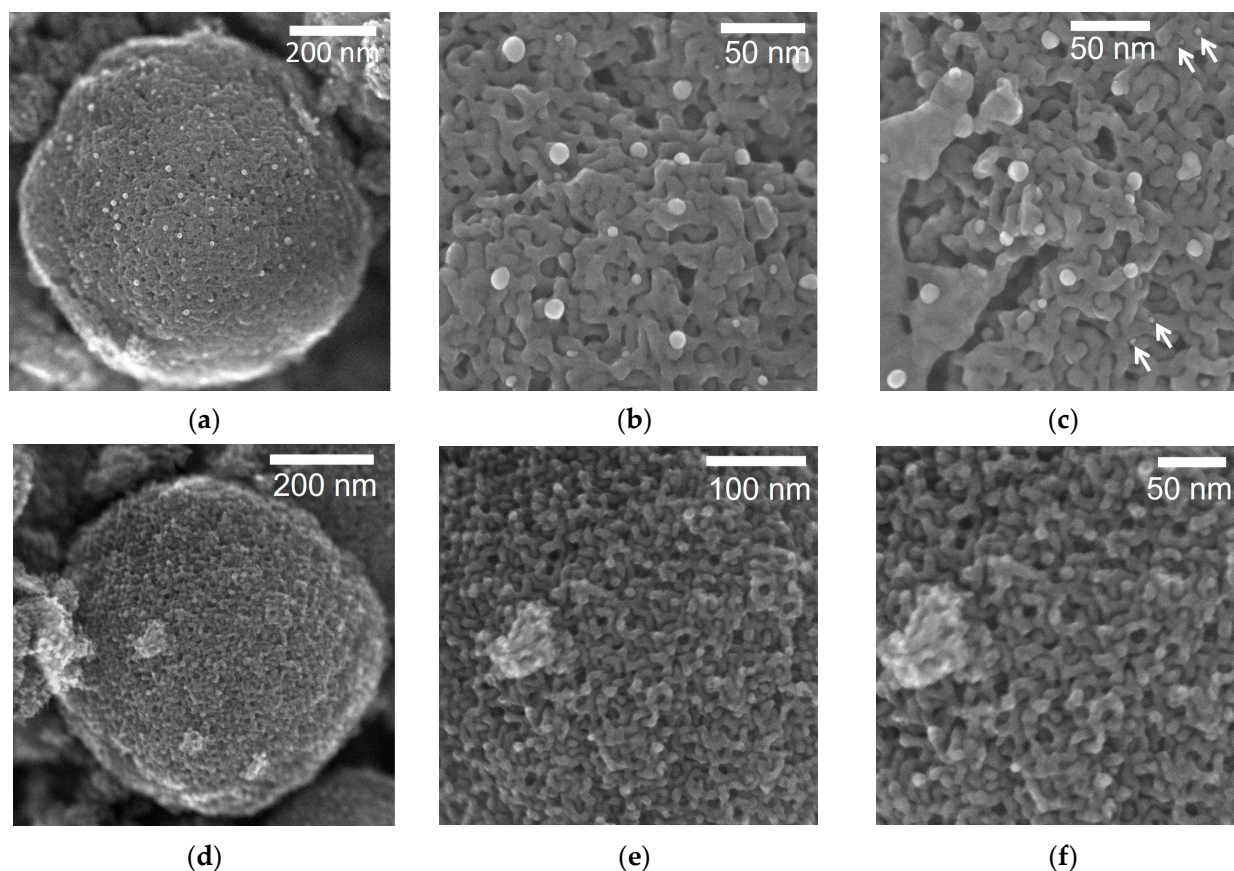


Figure 6. SE-STEM images of Au-Pd@meso-Co₃O₄ at lower magnification (a) and for two ROIs with higher magnification (b,c) as well as of meso-Co₃O₄ at different magnification (d–f) after gas measurements for 624 h at varied methane and propane concentrations at temperatures between 200 and 400 °C. Some small Au-Pd particles are indicated by arrows.

The Au-Pd particles are the main catalytic component in the Au-Pd@meso-Co₃O₄ catalyst, as seen by the comparison of catalytic activities with meso-Co₃O₄ (Figure 2 vs. Figure 3), although Co₃O₄ provides active sites for oxidation as well. The loss of catalytic activity of Au-Pd@meso-Co₃O₄ is correlated with the corresponding Au-Pd nanoparticle enlargement and the reduction of gas access to the nanoparticles inside the mesoporous structure due to the closure of pores at the surface. However, the instability of the mesoporous structure of Co₃O₄ contributes to common catalyst deactivation as well. One of the tasks of the support is the local stabilization of metallic nanoparticles. When the support itself is structurally not stable, it cannot sufficiently stabilize the particles, and an accelerated catalyst deactivation through particle sintering is expected [42].

However, in contrast to the Au-Pd@meso-Co₃O₄, the meso-Co₃O₄ support exhibits a lower degree of degradation (Figure 6d–f). The mesoporous structure is still intact, although a slight degradation of the mesoporous structure at the surface is also observed. The higher remaining specific surface area of meso-Co₃O₄ coincides with the higher remaining oxidation activity to methane. The strong adsorption of intermediates of propane oxidation (fouling) on the active sites explains well the higher degree of catalyst deactivation for propane oxidation [40]. Fouling can happen by testing with propane at low operating temperatures of 200 °C and 250 °C, where the catalyst is less active, and the oxidation process is not complete [36]. The fouling is not recognizable by the SE-STEM examination.

The morphology comparison of both aged catalysts (Figure 6) indicates that the presence of noble Au–Pd nanoparticles on meso- Co_3O_4 speeds up its aging through a sintering process. Accelerated aging of Au–Pd@meso- Co_3O_4 catalyst could be a result of the hot spots generated by agglomeration of the active phase [4]. The catalysts could be diluted with quartz to minimize the effect of hot spots initiating the sintering [11,12]. However, further factors could contribute to thermal aging. In the following, the reasons for the accelerated aging of the investigated catalysts are discussed, along with the mechanisms of sintering.

3.3. Mechanism of Thermal Deactivation of Catalysts

Thermal deactivation of supported precious metal catalysts by sintering process is usually problematic first at higher temperatures providing sufficient energy for atom or even crystallite mobilization, e.g., sintering of Pt/ Al_2O_3 catalyst can start at 600 °C [43]. Therefore, the question arises why the investigated Au–Pd@meso- Co_3O_4 exhibited such rapid sintering of both components, Au–Pd and meso- Co_3O_4 already at temperatures below 400 °C, which is in contrast to other reports dealing with similar catalysts [11].

The sintering process is driven by force directed to the minimization of high surface energy, which is typical for nanoparticles possessing a convex surface [19,44]. Additionally, nanostructured materials can feature an excess of Gibbs free energy ΔG due to a large proportion of interfaces and different defects [31,45]. The observed sintering reveals that the investigated 3D-ordered mesoporous morphology of Co_3O_4 is thermodynamically not stable as well. Apparently, there are many reasons for the lower stability of the Au–Pd@meso- Co_3O_4 catalyst.

The relative thermal stability of metals or metal oxides can be correlated in terms of the Hüttig ($T_{\text{Hüttig}}$) or Tamman (T_{Tamman}) temperatures, which are related to the absolute melting point (T_{mp} , in K). These temperatures can be used to estimate the vulnerability of the materials to sintering. Temperature drives the dissociation and diffusion of atoms of metals and oxides in the sintering process. The mean lattice vibration of atoms increases with higher temperatures. When $T_{\text{Hüttig}}$ ($0.3 T_{\text{mp}}$) is exceeded, less strongly bound surface atoms at defect sites can dissociate and diffuse easily across the surface. Above T_{Tamman} ($0.5 T_{\text{mp}}$), atoms in bulk become mobile [39]. Thus, surface diffusion starts at significantly lower temperatures than solid-state diffusion and materials with high surface area and high defect density are more prone to sintering.

A specific characteristic of the actual mesoporous structure of Co_3O_4 is the high surface-to-bulk ratio and a large proportion of interfaces and defects due to its nanocrystalline structure, causing a high surface energy [22]. Moreover, Co_3O_4 possesses a relatively low melting point of 895 °C [46], although some authors refer to a phase transformation of Co_3O_4 to CoO occurring at 900 °C [47–49]. Therefore, it is difficult to define $T_{\text{Hüttig}}$ and T_{Tamman} for Co_3O_4 . Nevertheless, the phase transformation taking place at quite low temperatures correlates with the lower thermodynamic stability of the structure. An extremely high amount of surface atoms and their high mobility make this structure prone to sintering, which was also observed particularly for Au–Pd@meso- Co_3O_4 , whereby Au–Pd particles affected the sintering rate of meso- Co_3O_4 . Simultaneously to support sintering, the sintering of metal particles was noticed. The presence of small and large Au–Pd particles at the same time on Au–Pd@meso- Co_3O_4 evidence metal particle sintering by atomic migration or Ostwald ripening, whereas larger particles grow at the expense of smaller ones by atom surface migration across support surface [20,38,40]. Due to comparably low operation temperatures applied during gas measurement experiments (≤ 400 °C), atomic migration is more probable than crystallite migration which requires higher thermal energy to induce the motion of larger crystallites. Moreover, mainly single particles of different sizes and hardly two touched particles were observed for Au–Pd@meso- Co_3O_4 . The Ostwald ripening is also identified by other authors as the most important mechanism of sintering at moderate temperatures (up to 750 °C) [50]. With regard to industrial applications, we investigated the catalyst with considerably higher metal content (7.5 wt%) as usually reported in the

literature (up to 3 wt%) [11]. Certainly, it is known that besides temperature and support features such as surface area, texture and porosity, the sintering rates are affected by metal type and metal loading on support [44]. The activation energy E_{act} for sintering decreases with increased metal loading [6,39,50]. Additionally, the high Au–Pd metal loading increases the surface temperature locally because of hot spot formation. Hot spots accelerate the sintering rate of the Co_3O_4 support (kinetic effect), which stringent mobility of surface atoms, in turn, intensifies the migration of metal atoms. The additional factor affecting the sintering of Au–Pd particles is the alloying of palladium ($T_{\text{mp}} = 1828 \text{ K}$) with gold, which has a considerably lower T_{mp} (1336 K). To improve the stability of nanoparticles the metal of higher T_{mp} should be used for alloying [10,51]. In addition, metal nanoparticles melt at significantly lower temperatures than the respective bulk material. For example, the melting point of 2 nm Au particles is about 600 K [44]. Regarding lower $T_{\text{hüttig}}$ it is conceivable that alloying with Au affects the metal atom mobility, reducing the thermal stability of Au–Pd particles and the entire long-term stability of the catalyst. In the work of Bechelany, et al., Au demonstrated very high mobility on Si surfaces already at 400 °C [52]. Therefore, Au is due to the high atomic migration apparently less appropriate for alloying for catalysts used at increased operation temperatures.

4. Conclusions

The investigation of the long-term stability of Au–Pd@meso- Co_3O_4 and meso- Co_3O_4 catalysts under sensor operation conditions reveals that both catalysts exhibit different deactivation behavior towards methane and propane oxidation. The different activity of both catalysts to methane and propane after performing long-term operations provides an argument for the presence of different reaction sites on the catalysts and their different susceptibility to deactivation processes taking place. The deactivation of Au–Pd@meso- Co_3O_4 is mainly due to occurred sintering. Thus, Co_3O_4 in Au–Pd@meso- Co_3O_4 catalyst lost to a high degree the access to its hollow mesoporous structure by the closure of pores at the surface. Furthermore, the size of Au–Pd particles significantly increased through Ostwald ripening when compared to their initial state. Since the nanostructure of Co_3O_4 in meso- Co_3O_4 support was less affected by the sintering process than in Au–Pd@meso- Co_3O_4 , which correlates with higher remaining oxidation activity, the promoting role of Au–Pd nanoparticles in the degradation of mesoporous Co_3O_4 support was identified. Nevertheless, the reasons for the high degradation of the Au–Pd@meso- Co_3O_4 catalyst are both the instability of the mesoporous structure of Co_3O_4 and the low stability of Au–Pd nanoparticles, owing to their high surface energy and low phase transformation temperature of Co_3O_4 enabling high mobility of surface atoms at low temperatures. The alloying of Pd with Au, which reveals even higher mobility, is an additional effect promoting the Ostwald ripening of metal nanoparticles. In conclusion, it can be stated that an Au–Pd@meso- Co_3O_4 catalyst is, despite its high catalytic activity, not suitable for long-term catalytic application at operation temperatures higher than 300 °C, owing to its low thermal stability. Thus, when designing new sustainable catalysts, the thermodynamical stability of all components must be considered.

Author Contributions: Conceptualization, O.Y. and K.S.; Formal analysis, X.L.; Funding acquisition, F.A. and J.W.; Investigation, X.L. and P.D.; Project administration, J.W. and K.S.; Supervision, J.W.; Writing—original draft, X.L. and O.Y.; Writing—review & editing, O.Y., P.D., F.A., J.W. and K.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was partially funded by the Fraunhofer Gesellschaft within the FluMEMS project and the Federal Ministry of Education and Research within the European funding program Eurostars in the project MEscal E! 113779.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available in this article.

Acknowledgments: The authors would like to thank Andreas Kürzinger (Fraunhofer IPM) for the assembly of the pellistors and Mickael Lejoyeux for the sample preparation for SE-STEM analysis.

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

References

- Gervasini, A.; Vezzoli, G.C.; Regaini, V. VOC removal by synergic effect of combustion catalyst and ozone. *Catal. Today* **1996**, *29*, 449–455. [\[CrossRef\]](#)
- Zhang, Z.; Jiang, Z.; Shangguan, W. Low-temperature catalysis for VOCs removal in technology and application: A state-of-the-art review. *Catal. Today* **2016**, *264*, 270–278. [\[CrossRef\]](#)
- Fernández, J.; Marín, P.; Díez, F.V.; Ordóñez, S. Coal mine ventilation air methane combustion in a catalytic reverse flow reactor: Influence of emission humidity. *Fuel Process. Technol.* **2015**, *133*, 202–209. [\[CrossRef\]](#)
- Cargnello, M.; Delgado Jaén, J.J.; Hernández Garrido, J.C.; Bakhtmutsky, K.; Montini, T.; Calvino Gámez, J.J.; Gorte, R.J.; Fornasiero, P. Exceptional activity for methane combustion over modular Pd@CeO₂ subunits on functionalized Al₂O₃. *Science* **2012**, *337*, 713–717. [\[CrossRef\]](#) [\[PubMed\]](#)
- Jiang, D.; Khivantsev, K.; Wang, Y. Low-Temperature Methane Oxidation for Efficient Emission Control in Natural Gas Vehicles: Pd and Beyond. *ACS Catal.* **2020**, *10*, 14304–14314. [\[CrossRef\]](#)
- Neyestanaki, A.K.; Klingstedt, F.; Salmi, T.; Murzin, D.Y. Deactivation of postcombustion catalysts, a review. *Fuel* **2004**, *83*, 395–408. [\[CrossRef\]](#)
- Wu, Z.; Deng, J.; Xie, S.; Yang, H.; Zhao, X.; Zhang, K.; Lin, H.; Dai, H.; Guo, G. Mesoporous Cr₂O₃-supported Au–Pd nanoparticles: High-performance catalysts for the oxidation of toluene. *Microporous Mesoporous Mater.* **2016**, *224*, 311–322. [\[CrossRef\]](#)
- Lee, D.-S.; Chen, Y.-W. The mutual promotional effect of Au–Pd/CeO₂ bimetallic catalysts on destruction of toluene. *J. Taiwan Inst. Chem. Eng.* **2013**, *44*, 40–44. [\[CrossRef\]](#)
- Xie, S.; Liu, Y.; Deng, J.; Zhao, X.; Yang, J.; Zhang, K.; Han, Z.; Arandiyán, H.; Dai, H. Effect of transition metal doping on the catalytic performance of Au–Pd/3DOM Mn₂O₃ for the oxidation of methane and o-xylene. *Appl. Catal. B Environ.* **2017**, *206*, 221–232. [\[CrossRef\]](#)
- Li, R.; Jin, B.; Ma, T.; Liang, Y.; Wei, Y.; Yu, X.; Li, J.; Liu, J.; Zhao, Z. Highly Efficient Catalysts of AuPd Alloy Nanoparticles Supported on 3D Ordered Macroporous Al₂O₃ for Soot Combustion. *ChemCatChem* **2022**, *624*, 118302. [\[CrossRef\]](#)
- Wu, Z.; Deng, J.; Liu, Y.; Xie, S.; Jiang, Y.; Zhao, X.; Yang, J.; Arandiyán, H.; Guo, G.; Dai, H. Three-dimensionally ordered mesoporous Co₃O₄-supported Au–Pd alloy nanoparticles: High-performance catalysts for methane combustion. *J. Catal.* **2015**, *332*, 13–24. [\[CrossRef\]](#)
- Wang, Z.; Deng, J.; Liu, Y.; Yang, H.; Xie, S.; Wu, Z.; Dai, H. Three-dimensionally ordered macroporous CoCr₂O₄-supported Au–Pd alloy nanoparticles: Highly active catalysts for methane combustion. *Catal. Today* **2017**, *281*, 467–476. [\[CrossRef\]](#)
- Li, X.; Liu, Y.; Deng, J.; Zhang, Y.; Xie, S.; Zhao, X.; Wang, Z.; Guo, G.; Dai, H. 3DOM LaMnAl₁₁O₁₉-supported AuPd alloy nanoparticles: Highly active catalysts for methane combustion in a continuous-flow microreactor. *Catal. Today* **2018**, *308*, 71–80. [\[CrossRef\]](#)
- Yang, N.; Liu, J.; Sun, Y.; Zhu, Y. Au@PdO_x with a PdO_x-rich shell and Au-rich core embedded in Co₃O₄ nanorods for catalytic combustion of methane. *Nanoscale* **2017**, *9*, 2123–2128. [\[CrossRef\]](#)
- Zheng, Y.; Yu, Y.; Zhou, H.; Huang, W.; Pu, Z. Combustion of lean methane over Co₃O₄ catalysts prepared with different cobalt precursors. *RSC Adv.* **2020**, *10*, 4490–4498. [\[CrossRef\]](#) [\[PubMed\]](#)
- Hu, L.; Peng, Q.; Li, Y. Low-temperature CH₄ Catalytic Combustion over Pd Catalyst Supported on Co₃O₄ Nanocrystals with Well-Defined Crystal Planes. *ChemCatChem* **2011**, *3*, 868–874. [\[CrossRef\]](#)
- Hu, L.; Peng, Q.; Li, Y. Selective Synthesis of Co₃O₄ Nanocrystal with Different Shape and Crystal Plane Effect on Catalytic Property for Methane Combustion. *J. Am. Chem. Soc.* **2008**, *130*, 16136–16137. [\[CrossRef\]](#) [\[PubMed\]](#)
- Ercolino, G.; Stelmachowski, P.; Grzybek, G.; Kotarba, A.; Specchia, S. Optimization of Pd catalysts supported on Co₃O₄ for low-temperature lean combustion of residual methane. *Appl. Catal. B Environ.* **2017**, *206*, 712–725. [\[CrossRef\]](#)
- Datye, A.K.; Votsmeier, M. Opportunities and challenges in the development of advanced materials for emission control catalysts. *Nat. Mater.* **2021**, *20*, 1049–1059. [\[CrossRef\]](#)
- Goodman, E.D.; Johnston-Peck, A.C.; Dietze, E.M.; Wrasman, C.J.; Hoffman, A.S.; Abild-Pedersen, F.; Bare, S.R.; Plessow, P.N.; Cargnello, M. Supported Catalyst Deactivation by Decomposition into Single Atoms Is Suppressed by Increasing Metal Loading. *Nat. Catal.* **2019**, *2*, 748–755. [\[CrossRef\]](#)
- Qu, Q.; Zhang, J.-H.; Wang, J.; Li, Q.-Y.; Xu, C.-W.; Lu, X. Three-dimensional ordered mesoporous Co₃O₄ enhanced by Pd for oxygen evolution reaction. *Sci. Rep.* **2017**, *7*, 41542. [\[CrossRef\]](#) [\[PubMed\]](#)
- Lyu, X.; Gao, H.; Diehle, P.; Altmann, F.; Tarantik, K.; Schmitt, K.; Wollenstein, J. Au-Pd@Meso-Co₃O₄: A Promising Material for New Generation Pellistor with Low Working Temperature. In Proceedings of the 2019 20th International Conference on Solid-State Sensors, Actuators and Microsystems & Eurosensors XXXIII (TRANSDUCERS & EUROSENSORS XXXIII), Berlin, Germany, 23–27 June 2019; pp. 1195–1198.

23. Lyu, X.; Gao, H.; Diehle, P.; Schmitt, K.; Tarantik, K.R.; Wöllenstein, J. Niedertemperatur-Pellistoren mit Au-Pd-impregniertem mesoporösem Co_3O_4 als katalytische Schicht: Pellistors with Au-Pd-impregnated mesoporous Co_3O_4 as a catalytic layer for low-temperature operation. *tm—Tech. Mess.* **2020**, *87*, 514–522. [\[CrossRef\]](#)
24. Miller, J.B. Catalytic sensors for monitoring explosive atmospheres. *IEEE Sens. J.* **2001**, *1*, 88–93. [\[CrossRef\]](#)
25. Dücső, C.; Ádám, M.; Fürjes, P.; Hirschfelder, M.; Kulinyi, S.; Bársony, I. Explosion-proof monitoring of hydrocarbons by mechanically stabilised, integrable calorimetric microsensors. *Sens. Actuators B* **2003**, *95*, 189–194. [\[CrossRef\]](#)
26. Lueptow, R.; Phillips, S. Acoustic sensor for determining combustion properties. *Meas. Sci. Technol.* **1994**, *5*, 1375–1381. [\[CrossRef\]](#)
27. Bársony, I.; Fürjes, P.; Ádám, M.; Dücső, C.; Vízváry, Z.; Zettner, J.; Stam, F. Thermal response of microfilament heaters in gas sensing. *Sens. Actuators B* **2004**, *103*, 442–447. [\[CrossRef\]](#)
28. Bierer, B.; Grgic, D.; Yurchenko, O.; Engel, L.; Pernau, H.; Reindl, L.; Wöllenstein, J. Wireless low-power warning system for the detection of flammable gases. In *Proceedings of the SMSI 2020 Conference; AMA Association for Sensors and Measurement*: Berlin, Germany, 2020; pp. 121–122. [\[CrossRef\]](#)
29. Bierer, B.; Grgić, D.; Yurchenko, O.; Engel, L.; Pernau, H.-F.; Jägle, M.; Reindl, L.; Wöllenstein, J. Low-power sensor node for the detection of methane and propane. *J. Sens. Sens. Syst.* **2021**, *10*, 185–191. [\[CrossRef\]](#)
30. Wang, Q.; Liu, J.; Li, Y.; Zhao, Z.; Song, W.; Wei, Y. Mesoporous Co_3O_4 supported Pt catalysts for low-temperature oxidation of acetylene. *RSC Adv.* **2017**, *7*, 18592–18600. [\[CrossRef\]](#)
31. Chen, J.; Zou, X.; Rui, Z.; Ji, H. Deactivation Mechanism, Countermeasures, and Enhanced CH_4 Oxidation Performance of Nickel/Cobalt Oxides. *Energy Technol.* **2020**, *8*, 1900641. [\[CrossRef\]](#)
32. Kleitz, F.; Choi, S.H.; Ryoo, R. Cubic Ia3d large mesoporous silica: Synthesis and replication to platinum nanowires, carbon nanorods and carbon nanotubes. *Chem. Commun.* **2003**, *17*, 2136–2137. [\[CrossRef\]](#) [\[PubMed\]](#)
33. 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. [\[CrossRef\]](#)
34. Xin, Y.; Wang, H.; Law, C.K. Kinetics of catalytic oxidation of methane, ethane and propane over palladium oxide. *Combust. Flame* **2014**, *161*, 1048–1054. [\[CrossRef\]](#)
35. Murata, K.; Ohyama, J.; Yamamoto, Y.; Arai, S.; Satsuma, A. Methane Combustion over $\text{Pd}/\text{Al}_2\text{O}_3$ Catalysts in the Presence of Water: Effects of Pd Particle Size and Alumina Crystalline Phase. *ACS Catal.* **2020**, *10*, 8149–8156. [\[CrossRef\]](#)
36. Finocchio, E.; Willey, R.J.; Busca, G.; Lorenzelli, V. FTIR studies on the selective oxidation and combustion of light hydrocarbons. *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 175–180. [\[CrossRef\]](#)
37. Ma, L.; Geng, Y.; Chen, X.; Yan, N.; Li, J.; Schwank, J.W. Reaction mechanism of propane oxidation over Co_3O_4 nanorods as rivals of platinum catalysts. *Chem. Eng. J.* **2020**, *402*, 125911. [\[CrossRef\]](#)
38. Bartholomew, C.H. Mechanisms of catalyst deactivation. *Appl. Catal. A* **2001**, *212*, 17–60. [\[CrossRef\]](#)
39. Argyle, M.D.; Bartholomew, C.H. Heterogeneous Catalyst Deactivation and Regeneration: A Review. *Catalysts* **2015**, *5*, 145–269. [\[CrossRef\]](#)
40. Moulijn, J.A.; van Diepen, A.E.; Kapteijn, F. Catalyst deactivation: Is it predictable? What to do? *Appl. Catal. A* **2001**, *212*, 3–16. [\[CrossRef\]](#)
41. He, B.J.-J.; Wang, C.-X.; Zheng, T.-T.; Zhao, Y.-K. Thermally Induced Deactivation and the Corresponding Strategies for Improving Durability in Automotive Three-Way Catalysts. *Johnson Matthey Technol. Rev.* **2016**, *60*, 196–203. [\[CrossRef\]](#)
42. Yang, X.; Li, Q.; Lu, E.; Wang, Z.; Gong, X.; Yu, Z.; Guo, Y.; Wang, L.; Guo, Y.; Zhan, W.; et al. Taming the stability of Pd active phases through a compartmentalizing strategy toward nanostructured catalyst supports. *Nat. Commun.* **2019**, *10*, 1611. [\[CrossRef\]](#) [\[PubMed\]](#)
43. Hofmann, G.; Rochet, A.; Ogel, E.; Casapu, M.; Ritter, S.; Ogurreck, M.; Grunwaldt, J.-D. Aging of a $\text{Pt}/\text{Al}_2\text{O}_3$ exhaust gas catalyst monitored by quasi in situ X-ray micro computed tomography. *RSC Adv.* **2015**, *5*, 6893–6905. [\[CrossRef\]](#)
44. Cao, A.; Lu, R.; Vesper, G. Stabilizing metal nanoparticles for heterogeneous catalysis. *Phys. Chem. Chem. Phys.* **2010**, *12*, 13499–13510. [\[CrossRef\]](#)
45. Andrievski, R.A. Review of thermal stability of nanomaterials. *J. Mater. Sci.* **2014**, *49*, 1449–1460. [\[CrossRef\]](#)
46. Ren, Y.; Cheng, Y.; Gorte, R.J.; Huang, K. Toward Stabilizing Co_3O_4 Nanoparticles as an Oxygen Reduction. *J. Electrochem. Soc.* **2017**, *164*, F3001–F3007. [\[CrossRef\]](#)
47. El-Shobaky, G.A.; Hewaidy, I.F.; Nabarawy, T. Sintering of non-stoichiometric NiO , CoO and Co_3O_4 catalysts. *Surf. Technol.* **1981**, *12*, 309–315. [\[CrossRef\]](#)
48. Mocala, K.; Navrotsky, A.; Sherman, D.M. High-temperature heat capacity of Co_3O_4 spinel: Thermally induced spin unpairing transition. *Phys. Chem. Miner.* **1992**, *19*, 88–95. [\[CrossRef\]](#)
49. Cardenas-Flechas, L.J.; Freire, P.T.C.; Paris, E.C.; Moreno, L.C.; Joya, M.R. Temperature-induced structural phase transformation in samples of Co_3O_4 and $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ for CoO . *Materialia* **2021**, *18*, 101155. [\[CrossRef\]](#)
50. Hansen, T.W.; Delariva, A.T.; Challa, S.R.; Datye, A.K. Sintering of catalytic nanoparticles: Particle migration or Ostwald ripening? *Acc. Chem. Res.* **2013**, *46*, 1720–1730. [\[CrossRef\]](#) [\[PubMed\]](#)

51. Cao, A.; Vesper, G. Exceptional high-temperature stability through distillation-like self-stabilization in bimetallic nanoparticles. *Nat. Mater.* **2010**, *9*, 75–81. [[CrossRef](#)]
52. Bechelany, M.; Maeder, X.; Riesterer, J.; Hankache, J.; Lerose, D.; Christiansen, S.; Michler, J.; Philippe, L. Synthesis Mechanisms of Organized Gold Nanoparticles: Influence of Annealing Temperature and Atmosphere. *Cryst. Growth Des.* **2010**, *10*, 587–596. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.