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Calorimetric methods for catalytic investigations of novel catalysts based on metallized S-layer preparations

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Abstract

The contribution will show the first results from calorimetric screening of novel catalysts. Biotemplated platinum nanoclusters were prepared on the basis of S-layer—bacterial surface proteins—on different supports. Methods were contrived and examined, permitting both the investigation of catalytic bulk material, and the investigation of sensory interesting coatings. The calorimetric measurements were carried out using conventional calorimetric technique (DSC 111, firm SETARAM) and miniaturized calorimetric systems (integrated circuit calorimeter – IC-calorimeter and a sensor platform). The results of the calorimetric investigations to the selected model reactions (oxidation of hydrogen, carbon monoxide and propane) demonstrate the interesting characteristics of these new catalysts.

Keywords: Catalytic activity; Metallized S-layer; Miniaturized calorimeter; Biotemplating

1. Introduction

The investigated platinum nanoclusters were prepared based on biotemplating by bacterial surface layer proteins (S-layer) of *Bacillus sphaericus*. The S-layer proteins are the most commonly observed cell surface structures in prokaryotic organisms. Isolated S-layer proteins have the intrinsic tendency to self-assemble into two-dimensional arrays in suspensions and at different kind of interfaces [1]. This biological templating is a novel approach for the creation of molecular engineered nanostructures with the advantages of well-defined structural, chemical and physical properties [2]. Self-assembly and recrystallization of S-layer proteins on solid substrates are discussed in literature [3] and imaged by atomic force microscopy [4]. The highly repetitive surface structure and the possibility for combining S-layer lattices with other functional molecules makes them very interesting in nanotechnology, for instance to fabricate metallic/semiconducting nanostructures and arrays [5] or biomimetrics [6]. The small clusters and the inherent repeating patterns of bacterial S-layer proteins indicate the possibility of high catalytic activity of such preparations. The formation of regular metallic nanoparticles on bacterial surface layers was studied with transmission electron microscopy (TEM) [7]. In order to stabilise the particles and prevent agglomeration the authors use catalyst supports [8].

Calorimetry has been recognized as a powerful and universal tool for the investigation of catalysts. The results of calorimetric studies provide important contributions for the characterisation of various catalysts, including initial performance, stability or deactivation processes. The choice of the calorimetric measuring technique permits thereby the investigation of catalysts for gaseous phase reactions [9–11], as also for conversions in the liquid phase [12].

Our calorimetric measurements were performed using the oxidation reactions of hydrogen, carbon monoxide and propane. These reactions carry a model character, in particular because of the interesting temperature range of their catalytic effectiveness. Furthermore, these systems are of great technical importance for various applications, for instance the hydrogen- and CO-sensor technology, catalytic converters in automotive catalysis, or industrial syntheses.

For the characterization of the catalytic activity of the above-mentioned S-layer preparations, we had to contrive a technique and measuring regime, using a conventional calorimeter. This

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method had to be adjusted to the miniaturized systems using catalytic coatings. First, the IC-calorimeter was used, which is a approved system for investigation of various gaseous-solid reaction [13,14]. Furthermore, a promising new arrangement, using a sensor platform from the firm *Heraeus*, is presented in the contribution.

2. Experimental

Bacterial surface protein from *Bacillus sphaericus* was employed as a suspension of assemblates in a 50 mM Trishydroxymethylaminomethane/H_2SO_4 buffer solution at pH 7.4 with a final concentration of ≈10 mg/ml. The 3 mM $K_2[PtCl_4]$ solution was aged in the dark at ambient temperature for at least 1 day to allow for complex equation prior to sample preparation.

To prepare sample type **A**, an appropriate amount of protein was activated with the metal complex solution, e.g. 50 μl protein suspension were incubated with 1.71 ml $K_2[PtCl_4]$ solution in the dark for 24 h. Thereafter, γ-alumina powder (e.g. 200 mg) was added. While mixing the Pt^{2+} was reduced by addition of dimethylaminoborane (e.g. 450 μl of 15 mM DMAB). Although generally DMAB reduces Pt^{2+} rapidly, the solution was mixed for some more hours.

For sample **B**, 50 μl protein suspension in 50 mM phosphate buffer pH 7.4 and 3 mM NaN_3 were incubated with 1.71 ml $K_2[PtCl_4]$ solution for 24 h. To immobilize the metalized S-layer on substrate, the solution was mixed with 200 mg γ-alumina powder for 24 h.

The protein-free reference sample **C** has been prepared by mixing 1.6 ml $K_2[PtCl_4]$ solution with 20 mg alumina powder for 24 h and thereafter reducing by addition of 1 ml 5 mM DMAB.

Sample **D** has been prepared similar to sample **B**, but using 100 mg of porous silicon carbide particles as support.

At the end in all preparations sedimentation was employed to separate unbound components by discarding the supernatant. The catalyst powders were washed three times with deionized water and finally dried at 45 °C for 1 day.

The platinum content was determined using inductive coupled plasma-atomic emission spectroscopy. Therefore, all platinum contained in a catalyst sample has been solved with *aqua regia* prior to measurement. The platinum contents established were 3.9% (**A1**), 3% (**A2**), 1.5% (**A3**), 0.45% (**A4**), 0.38% (**B**), 3.7% (**C**) and 0.26% (**D**), respectively.

The catalytic activity of platinum S-layer from different preparations was investigated with three calorimetric arrangements:

- a reactor consisting of quartz tubes, assembled in a DSC 111 from the firm *Setaram*;
- an IC (integrated circuit) calorimeter [15];
- a sensor platform from the Firm *Heraeus* [16].

The DSC 111 is a conventional scanning calorimeter, which can be used for manifold applications. Because of its wide temperature range it is possible to measure the catalytic activity for a multitude of different test reactions, like H_2, CO, C_3H_8, CH_4.

The used quartz tube reactor consists of two quartz tubes, vertically arranged in the oven of the DSC 111. In the quartz tube a frit is embedded. The catalyst (bulk) is located on the frit. The different gases for the oxidation reactions were dosed by mass flow controllers (MFC). Then a defined composition flows through the catalyst in the quartz tube. Afterwards the same gas flow passes the empty tube, the reference. This simple gas flow can be used because of the small changes in gas composition during reaction and the stationary measurement. The schematic measurement assembly is shown in Fig. 1.

For the investigation of the catalytic activity of the sample the catalytic conversion in dependence of the temperature is from particular interest. We have used isothermal stages. The temperature was kept constant (9000 s). In this time the composition of the gas is changed between the reaction mixture (both reaction components, e.g. carbon monoxide and oxygen, 4500 s) for measuring the thermal power from the catalytic reaction, and pure oxygen for detecting the baseline. The resultant thermal power is proportional to the catalytic activity of the sample. The dependency of the catalytic activity from the temperature is always determined by measuring from the highest to the lowest temperature with a step range of 10 K.

In contrast to the bulk probes, analysed with the DSC 111, catalytic coatings were investigated in the IC calorimeter. The assembly of the calorimeter chip is described in [15].

The gas, which is dosed by mass flow controllers outside of the IC calorimeter, is brought in the reaction chamber by tubes and capillary. The regime of the measurement with different isothermal steps, where the composition of the gas is varied, can be adopted from the DSC 111. Measurements were taken with decreasing temperature. Here, the catalytic reaction takes place only at the surface of the catalytic coating, in contrast to the measurements of catalytic bulk preparations, where the gas flows through the sample.

The investigation of catalytic coatings with the IC-calorimeter can be carried out uncomplicated with a low apparatus effort and a small amount of material. The preparation of the coating was made in analogy to the well-known enzyme immobilisation for thick-film biosensors with glutardialdehyde [16].

The chip carrier allows to measure in a temperature range between 250 and 400 K [15]. For calculating the thermal power P from the thermo voltage U_{th}, detected by the thermopiles at the chip, a correlation factor, the sensitivity (V/W) is needed. The sensitivity is determined by electrical calibration and varies from chip to chip (2.0–2.5 V/W). The sensitivity for each thermopile chip is relatively constant in the temperature range of 290–350 K. A further increasing of measuring temperature is not useful because of the strong decreasing of the sensitivity.

A second possibility to investigate catalytic coatings calorimetrically is a sensor platform, consisting of platinum resistance thermometer Pt 1000, made by the firm *Heraeus* [17]. Fig. 2 shows schematically this sensor system. In this arrangement the reaction chamber with the two sensor platforms is surrounded by an oven (1) and different heat shields (2). By meaning of a twin system one of the sensor platform is coated with the cat-

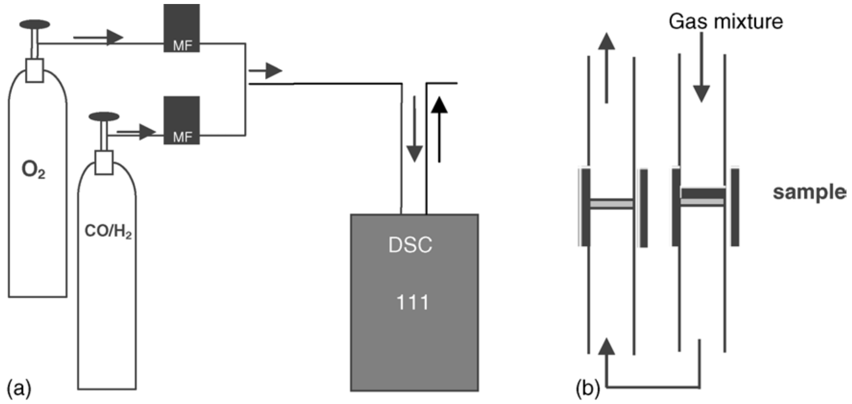

Fig. 1. (a) Mixing of the different gases, (b) Gas flow within the quartz tube reactor.

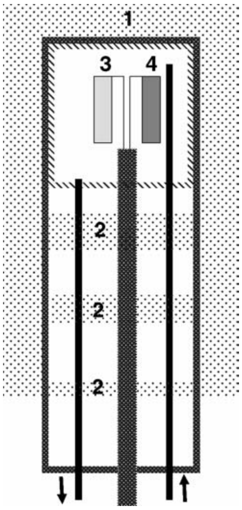

Fig. 2. Arrangement of the sensor platform.

alytic active sample (3), the other one acts as the reference (4). The gas mixture enters the reaction chamber through capillaries and overflows the sensors.

3. Results

3.1. Results of measurements in the DSC 111

From the wide range of catalysed reactions, which can be investigated with the DSC 111, three oxidations are chosen:

- The oxidation of hydrogen

  $H_2 + 0.5O_2 \rightarrow H_2O(g)$

- The oxidation of carbon monoxide

  $CO + 0.5O_2 \rightarrow CO_2$

- The oxidation of propane

  $C_3H_8 + 5O_2 \rightarrow 4H_2O(g) + 3CO_2$

Fig. 3 shows results from measurements with catalytic bulks in the quartz tube reactor of the DSC 111. In these diagrams the dependency of the detected thermal power from the temperature is illustrated. The conversion was calculated from the relation of the measured thermal power P to the theoretical thermal power P_{th}.

$$P_{\mathrm{th}} = \frac{\mathrm{d}q_{\mathrm{th}}}{\mathrm{d}t} = \frac{\mathrm{d}n_{\mathrm{A}}}{\mathrm{d}t} \times \Delta_{\mathrm{R}} H_{\mathrm{A}}(T)$$

t is the time, q_{th} is theoretical heat, $\Delta_{\mathrm{R}} H_{\mathrm{A}}$ is the molar reaction enthalpy, calculated using data from the data base HSC 4 in dependence of temperature and gas A, n_{A} is the amount of gas A, calculated from the gas flow, A, used gases: H_2, CO, C_3H_8.

The results of calorimetric measurements (Fig. 3) using various catalytic reactions show that the conventional calorimeter DSC 111 is very well suitable for the investigation of catalytic bulk preparations in a wide temperature range. In particular, the illustrations demonstrate the interesting possibilities of the calorimetric investigations for the optimization of the catalytic features of biotemplated preparations.

The influence of the used support for the CO-oxidation is presented in the Fig. 3a. Characteristic for the carbon monoxide oxidation is the noticeable jump in the thermal power respectively to the conversion rate at a certain temperature. This remarkable temperature can be very well used for the characterisation of the influence of different supports for the catalytic properties, beside the well-known catalytic feature T_{50} (temperature at which the half conversion is reached). Preparations on silicon carbide have 20 K lower temperatures for start of catalytic activity (jump) or T_{50} value, but we have to use a higher sample mass for detecting this catalytical activity.

Furthermore, the DSC-curves using the catalyst probes on Al_2O_3 are better reproducible. We assume a sample size effect, because of the more non-uniform SiC-particles than the Al_2O_3 powder. The question about the catalytic species (Pt/Pt oxide) could not be clarified by these first measurements yet. In addition, further systematic thermal investigations are necessary, whose results and insights open an excellent possibility for the optimization of the catalytic activity of these new catalysts.

A comparative view of differently prepared Pt catalysts on Al_2O_3 support is given in Fig. 3b. For this comparison the catalytic propane oxidation (temperature range >150 °C) was used.

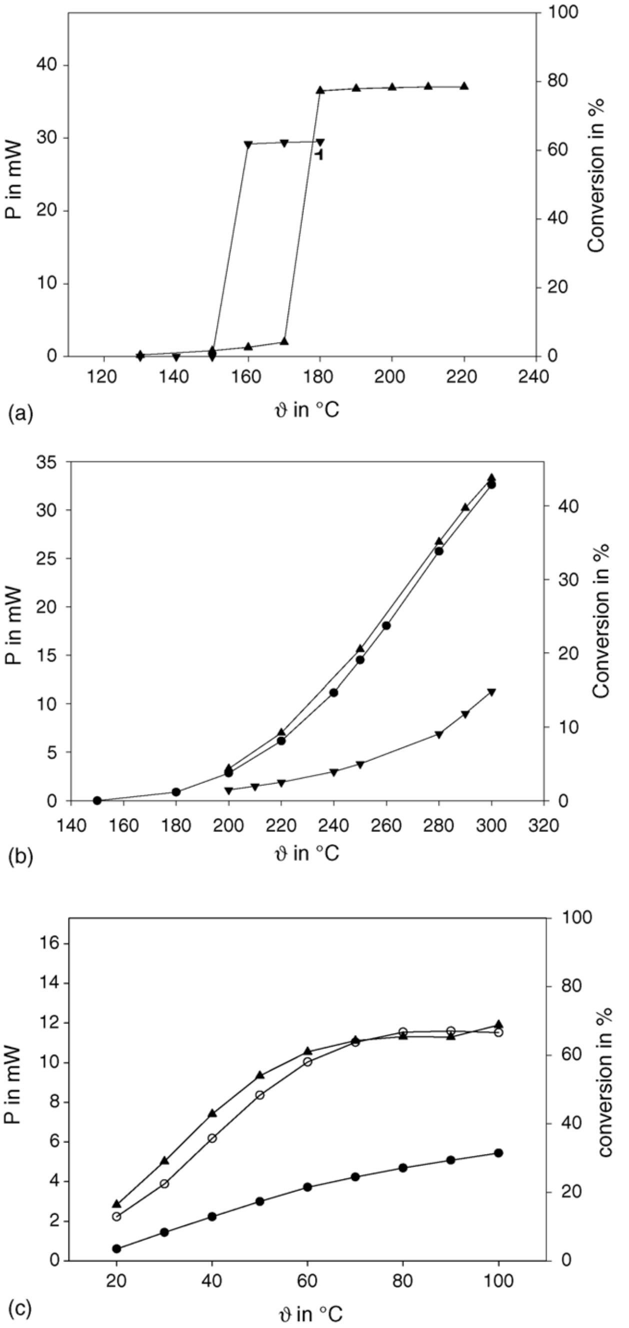

Fig. 3. Results of measurements using the DSC 111. (a) Catalytic oxidation of carbon monoxide (gas flow: 5 ml/min, CO: 4.8 vol%) with Pt S-layer on different carrier: (▼) silicon carbide (D); Pt in the bulk ∼56 μg; (▲) aluminium oxide (B); Pt in the bulk ∼14 μg. (b) Catalytic oxidation of propane (gas flow: 5 ml/min, C_3H_8 1 vol%, Pt in the bulk ∼85 μg) with different catalysts: (●) Pt S-layer on aluminium oxide (A1); (▲) Pt on aluminium oxide, without S-layer (C); (▼) Commercial catalysts F221 from the firm Degussa, Pt on aluminium oxide. (c) Catalytic oxidation of hydrogen (gas flow: 5 ml/min, H_2: 2 vol%) with Pt S-layer on aluminium oxide (A4). (●) after 2 h at 170 °C, oxygen atmosphere, (○) after 2 h at 170 °C, hydrogen atmosphere, (▲) after 2 h at 300 °C, oxygen atmosphere.

The catalytic activity of the S-layer based Pt catalyst is comparable with a platinum catalyst on aluminium oxide (without S-layer) as a reference system. An industrial used platinum catalyst has a significant lower activity in the considered temperature range for the chosen oxidation reaction.

Some results of the third studied catalytic reaction, the oxidation of hydrogen, are depicted in Fig. 3c. With these measurements the influence of the pre-treatment on the catalytic activity should be investigated. The sample evolves its highest catalytic activity after exposure to hydrogen, a reducing gas, for 2 h at 170 °C.

3.2. *Results of the measurements with the IC calorimeter*

Results of the investigations with catalytic coatings are presented in this section. As initially described, the aim of the IC calorimeter development was a miniaturisation of the arrangement, a reduction of the necessary sample quantities and sensory applications. We have to prove the catalytic activities realised on the very small sensitive area (4 mm × 4 mm) of our IC calorimeter. We adjusted the measuring regime from the conventional arrangement (DSC 111) to the IC calorimeter.

For the sensor application of the IC calorimeter in gas analytics catalytically active coatings are necessary, which ensure a large long-term stability, small catalyst quantities and reproducible results of measurement. The reproducibility for the investigations of the catalytic hydrogen oxidation is shown in the Fig. 4. The percentage of conversion, calculated from the measured and theoretical thermopile voltage U_{th} is given in relation to the temperature. The catalytic activities realized on the chip were sufficient for the conversion of approx. 80% (temperature 80 °C) of the used hydrogen. In comparison the coating with Pt-black shows at the same temperature only approx. 30% conversion. The dependence of the measured thermopile voltage from the concentration of hydrogen is presented in Fig. 5. The subject of future investigations is the further optimization of the preparation of catalytic coatings and the determination of the analytic detection limit using metallised S-layer preparations.

3.3. *Results of the measurements with the sensor platform*

To avoid the disadvantage of the temperature limitation of the IC calorimeter (80 °C), catalytic coatings can also be inves-

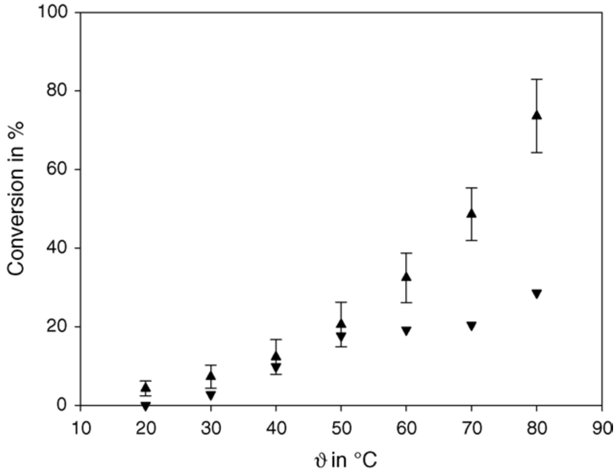

Fig. 4. Results of measurements with a coated thermopile chip—immobilised Pt-S-layer on Al_2O_3 (A3, (▲)) compared with Pt-black catalyst coating (▼). Catalytic H_2 oxidation, gas flow 5 ml/min, 1 vol%.

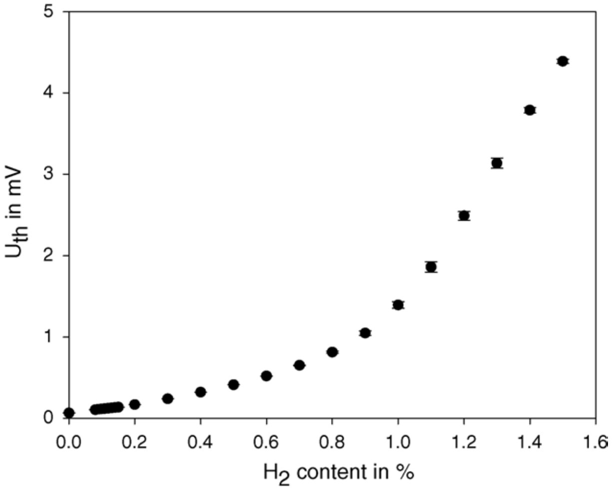

Fig. 5. Dependence of thermo voltage from the hydrogen concentration at a temperature of 60 °C. Immobilised Pt-S-layer on Al_2O_3 (B).

tigated by the sensor platform, based on Pt 1000 resistance thermometer from Hereaus [18]. The specification of the Pt 1000 permits measurements in the temperature range between −50 and +450 °C [19].

First measurements with the sensor platform were made of a catalytic coating with platinum on aluminium oxide for the oxidation of hydrogen to demonstrate the usability of this arrangement. Fig. 6 shows a measurement at 90 °C with gas mixture containing hydrogen and oxygen (impulse 2 min). The presented curve is the difference curve between the signals of the sample (coated) and reference sensor.

The CO-oxidation at a temperature of 200 °C was used for first measurements with Pt-S-layer. The Pt-S-layer-Al_2O_3 preparation were immobilized on the sensor platform with glutardialdehyde [16]. Fig. 7 shows a linear correlation of the difference signal and the CO-concentration. The realized catalytic activities on the sensor platform were sufficient for an almost complete conversion of carbon monoxide. The coatings could be used up to a temperature of 300 °C. Here further optimization is necessary regarding sample addition, stability of the coating and the gas area.

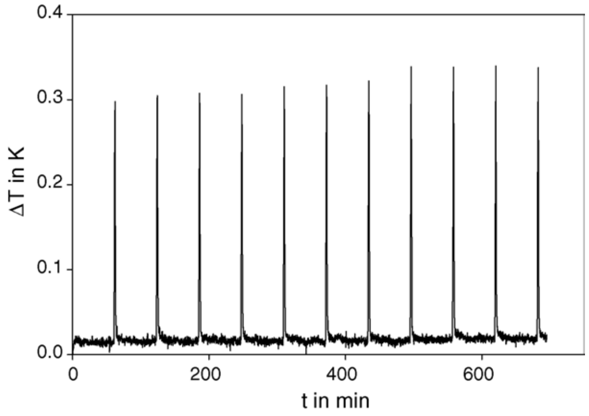

Fig. 6. Results of the hydrogen oxidation, concentration of hydrogen: 2.5 vol%, flow rate 5 ml/min.

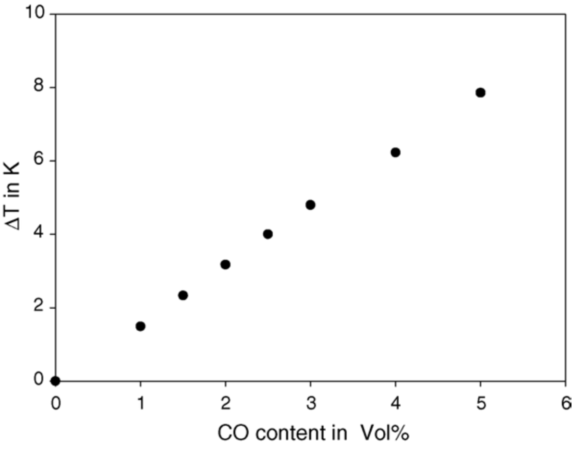

Fig. 7. Results of carbon monoxide oxidation, flow rate: 5 ml/min (A2).

4. Summary

The results of the different arrangements show the high potentialities of calorimetric measurements to investigate catalytic activities and to optimise catalytic preparations. The novel catalytic preparations on the basis of S-layer biotemplated platinum nanoclusters prove to be very useful catalysts both in the form of catalytic bulk and sensitive coating at thermal sensors for determination of various gas compositions. The results of the various calorimetric methods confirm the expected high catalytic activity of the biotemplated catalysts especially by using comparatively low temperatures. The kind of support, the pretreatment steps of the catalyst preparation and the kind of the metallisation are of crucial importance for an optimisation of the catalytic activity of the preparations.

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