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## A highly sensitive technique for detecting catalytically active nanoparticles against a background of general workplace aerosols

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**Abstract.** A new measurement technique was studied using catalysis to specifically detect airborne nanoparticles in presence of background particles in the workplace air. Catalytically active nanoparticles produced by spark discharge were used as aerosol catalysts. According to these particles suitable catalytic test reactions were chosen and investigated by two different approaches: catalysis on airborne nanoparticles and catalysis on deposited nanoparticles. The results indicate that catalysis is applicable for the specific measurement of nanoparticles in the workplace air. Catalysis on airborne particles is suitable for the specific detection of very active nanoparticles, e.g. platinum or nickel, at high concentrations of about  $10^7$  #/cm<sup>3</sup>. The approach of catalysis on deposited particles is better suited for nanoparticle aerosols at low concentrations, for slow catalytic reactions or less active nanoparticles like iron oxide (Fe<sub>2</sub>O<sub>3</sub>). On the basis of the experimental results detection limits in the range of µg or even ng were calculated which assure the good potential of catalysis for the specific detection of nanoparticles in the workplace air based on their catalytic activity.

### 1. Introduction

The inhalation of nanoparticles is considered to be the primary route of exposure to engineered nanoparticles (ENP) in the workplace [1]. However, a quantitative exposure assessment depends strongly on the exposure scenario. Airborne ENP in the environment as well as in workplace air are normally mixed with background particles. The concentration and the composition of these background particles depend on the location and the operations which are carried out in the workplace [2,3] and may be higher than the ENP concentration [4]. Aside from difficulties in isolating the ENP contribution to the total concentration, another uncertainty arises from the possible adhesion of ENP to the background aerosol particles due to coagulation [5], and the resulting disappearance of these particles from the size distribution.

A variety of devices is available to measure the particle size distribution, the number or mass concentration and the specific surface area of nanoparticles in workplace air [6,7]. However, these techniques are not generally capable of distinguishing between a target ENP and the background particles of the workplace [8-10]. Furthermore, the determination of particle properties such as the morphology or the chemical composition requires off-line techniques for physical or chemical

analysis. New, material specific on-line analytical methods are therefore needed to identify ENP in background aerosols.

Catalysis offers significant potential for the substance-specific detection of catalytically active particles as well as for the discrimination of trace amounts of such airborne ENP against an inactive background aerosol. In [11] and [12] it is shown that metal nanoparticles like palladium and nickel supported on SiO<sub>2</sub> or TiO<sub>2</sub> are still catalytically active. In the case of palladium the supports have nearly no influence on the catalytic behaviour of the particles. So we assume that ENP can be detected via their catalytic activity even if they are coagulated with the background particles of the workplace. We therefore report preliminary results of an investigation into the suitability of such a technique for measuring the catalytic activity of engineered catalyst nanoparticles, both in their airborne state and after deposition from the aerosol onto a substrate. The experiments reported below were conducted with known amounts of freshly generated aerosol with a precisely known size distribution, which were exposed for defined amounts of time to gaseous educts; the gaseous reaction products were detected by infrared spectroscopy. On the basis of these measurements we give first estimates of the sensitivity of the technique for several materials and demonstrate that it is indeed possible to very rapidly detect very small amounts of nanoaerosols on the basis of their activity. In Section 2 we describe our choices of ENP material and the corresponding chemical model reactions. Section 3 contains the methods of catalyst particle preparation and the experimental setup for measuring their activity. Section 4 presents experimental results and calculated detection limits. Finally Section 5 concludes and points out future work.

## 2. Model Reactions

A well understood chemical reaction was selected for each of several industrially relevant catalyst substances according to the following criteria: Both educts and reaction products should be gaseous; the sensitivity and rate of the reaction should be as high as possible in order to achieve low detection limits.

### 2.1. Oxidation of H<sub>2</sub> over platinum: $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$

The catalytic oxidation of hydrogen over platinum nanoparticles is very fast [13]. The reaction already takes place at ambient air temperature and is therefore at best suitable for the detection of platinum at workplaces. The catalytic activity of the platinum during the oxidation of H<sub>2</sub> is known to depend on the primary particle size of the platinum agglomerates [14].

### 2.2. Methanation of CO over nickel: $\text{CO} + 3 \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$

The formation of methane from carbon monoxide and hydrogen over nickel nanoparticles represents a rather slow catalytic reaction [15] however reaching sufficient velocity at elevated temperature. The maximum catalytic activity was observed at 450°C [12]. Nickel catalysts have a high selectivity to the formation of methane so this model reaction shows good potential for the specific detection of nickel nanoparticles in the workplace air. However, the catalytic behaviour of nickel is also dependent on the primary particle size of the nickel agglomerates.

### 2.3. Oxidation of CO over iron oxide (Fe<sub>2</sub>O<sub>3</sub>): $2 \text{CO} + \text{O}_2 \rightarrow 2 \text{CO}_2$

The CO oxidation represents a catalytic reaction which is catalyzed by oxidic nanoparticles. It is a well researched reaction due to its importance for fuel cells, with an activity maximum at 300°C and a primary particle size of the iron oxide agglomerates of 3 nm [16].

### 2.4. Hydrogenation of ethene over palladium: $\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$

Palladium nanoparticles are frequently used in hydrogenation or dehydrogenation reactions of hydrocarbons. Especially the hydrogenation of ethene is an extensively studied catalytic reaction [11] which already runs at ambient air temperature. It was therefore chosen as a model reaction specific to

the detection of palladium. As with the other materials, the catalytic activity of palladium is dependent on the primary particle size of the metal [17].

### 3. Experimental Procedures

Nano-aerosols of the above mentioned materials were produced by a spark discharge technique described frequently in the literature [18,19]. These aerosols had very well defined concentrations and particle morphologies. The catalytic activity of the nanoparticles was then measured directly in the aerosol stream by adding educt gases or – in the case of less active materials and slower reactions – by first depositing the particles onto filters. Details of these techniques are described below.

#### 3.1. Catalyst preparation and characterization

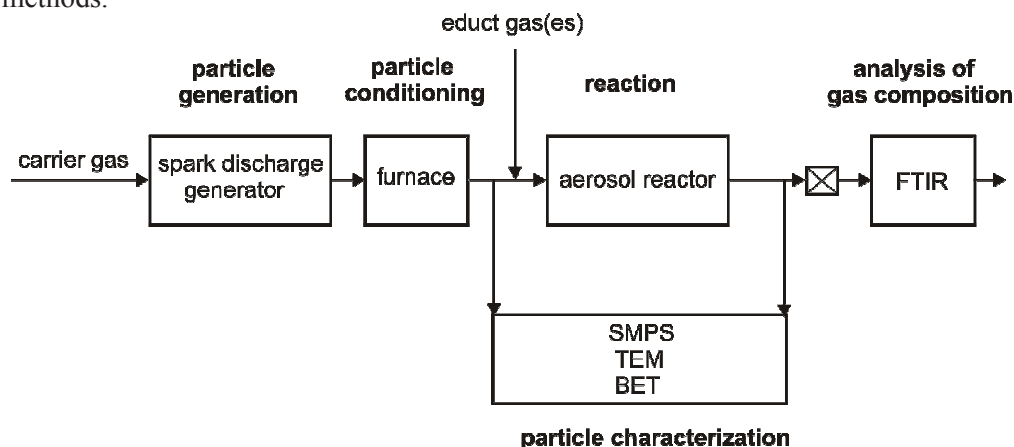
Catalyst nanoparticles of nickel, platinum, palladium, and iron were produced in a spark discharge generator using high purity electrodes of the desired material. The carrier gas was nitrogen with a purity of 99.99% or a 4:1 mixture of Ar and O<sub>2</sub> with a purity of 99.5%, each at a flow rate of 1.0 liter/min. The addition of O<sub>2</sub> oxidizes the iron nanoparticles to Fe<sub>2</sub>O<sub>3</sub>. All flow rates were controlled by mass flow controllers (MKS, Brooks).

In the spark discharge, relatively uniform primary particles, usually in the size range of a few nanometers, are formed by homogeneous nucleation of small amounts of metal vapour ejected from the electrodes during the discharge. These primary particles rapidly undergo collisions to form agglomerates which can additionally be sintered in the aerosol state in a second process step, if so desired, to modify their structure in defined ways.

The catalyst aerosols were characterized on-line using an electrical mobility spectrometer (SMPS, TSI 3071A and 3775) to provide information about the mobility size distribution and concentration of the agglomerates. The diameters of the primary particles as well as the shape of the agglomerates were determined by transmission electron microscopy (TEM, Philips CM12, 120 kV). The surface area was measured by nitrogen BET (Quantachrome Nova 1200). (Note that the morphological characterization of the agglomerates does not take any size changes occurring at elevated temperatures into account. This issue is well understood, but not addressed in this paper.)

#### 3.2. Catalysis on airborne nanoparticles

Catalysis on airborne nanoparticles - also known as “aerosol catalysis” [14,15,20] - offers the possibility to determine the catalytic activity of nanoparticles on very short time scales in the range of seconds to minutes. It is therefore a true on-line technique for measurements of the catalytic activity of ENP. In addition the method requires only small catalyst mass concentrations in the order of ng/cm<sup>3</sup>. Another advantage is the avoidance of artefacts due to contamination occurring more commonly in off-line methods.



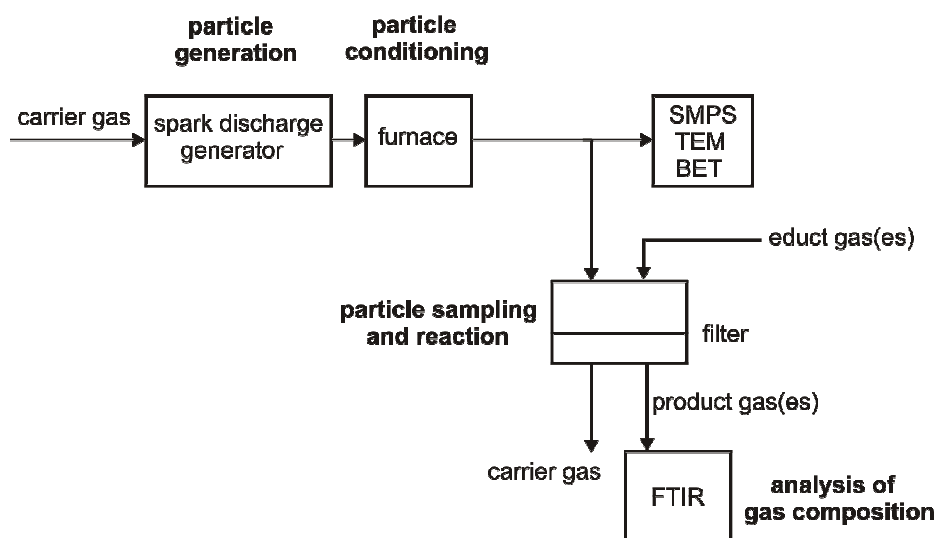
**Figure 1.** Schematic diagram of the experimental setup for measuring the catalytic activity and structure of airborne nanoparticles.

Figure 1 shows a schematic diagram of the experimental setup used for catalysis on airborne nanoparticles and for structural analysis. Following its generation in the spark discharge generator and any structural modifications, the educt gases are added to the aerosol before entering a heated glass reactor where the catalytic reaction is initiated. The concentration of gas phase products generated from the reaction is monitored online with a FTIR Spectrometer (Bruker Vector 22) equipped with a cell of suitable path length depending on their concentration. A particle filter just upstream of the cells protects the mirrors from particle deposition. It was determined that this filter and any particles deposited on it over time have no influence on the gas composition.

### 3.3. Catalysis on deposited nanoparticles

By sampling the nanoaerosol on a filter prior to running the catalytic reaction, it is possible to accumulate small amounts of catalyst material (in the order of micrograms). This approach is better suited for ENP aerosols at low concentrations, for slow catalytic reactions and/or less active ENP. The catalytic activity is nevertheless determined on-line, in the sense that educt gases are added directly to the filter, thereby avoiding filter handling and potential contaminations of the sample by exposure to ambient air.

A schematic diagram of the experimental setup for catalysis on deposited nanoparticles is shown in Figure 2. Catalyst aerosols are produced by spark discharge as before and then sampled onto a 37 mm diameter glass fiber filter (Machery-Nagel) placed downstream of the spark discharge generator. After sampling a defined amount of aerosol, the carrier gas is switched off and pre-mixed educt gases are added. If necessary the filter housing is heated to initiate the catalytic reaction. The deposited mass of ENP material is determined gravimetrically. The gas phase products of the catalytic reaction are also detected by FTIR. As before, the nanoaerosols are characterized on-line by SMPS, and off-line by TEM and BET for concentration, size and particle morphology.



**Figure 2.** Schematic diagram of the experimental setup for measuring the catalytic activity and structure of deposited nanoparticles.

## 4. Results and Discussion

The results of the catalyst preparation and the catalytic experiments on airborne as well as on deposited nanoparticles are presented in the following. The turn-over frequency (TOF) was used as a measure for the catalytic activity of particles. Where possible, it was calculated as a function of the number of product molecules produced per time and per number of active sites. (Note that the active sites per unit surface area were not experimentally investigated values but literature data). At the end of the chapter a summary of calculated detection limits for each catalyst is presented.

#### 4.1. Catalysis on airborne nanoparticles

4.1.1. *Oxidation of H<sub>2</sub> over platinum.* The platinum agglomerates (Figure 3) produced by spark discharge had primary particle diameters in the range of 5 nm and a BET surface area of 58 m<sup>2</sup>/g. The particle number concentration in the aerosol immediately downstream of the spark discharge generator was very stable in the range of 10<sup>7</sup> agglomerates per cm<sup>3</sup>; the corresponding mass concentration  $c_{m,Pt}$  was determined gravimetrically to 56 ng/cm<sup>3</sup>.

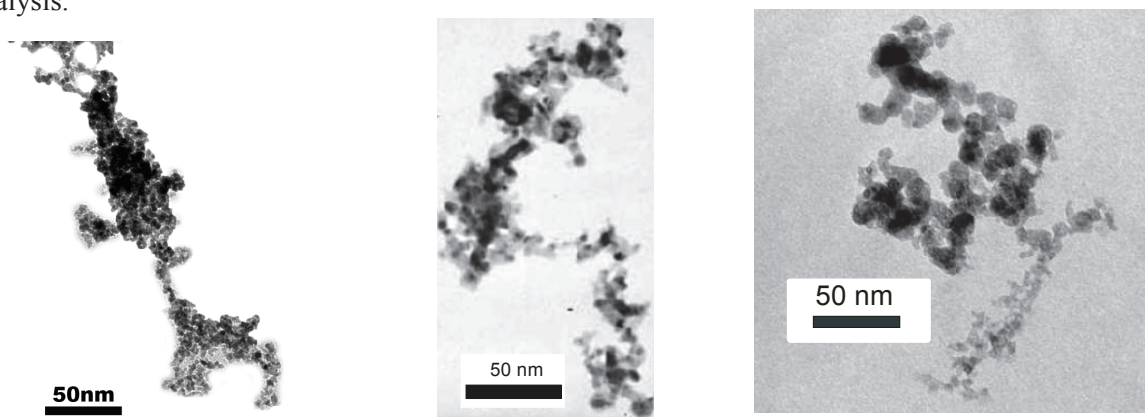
To initiate the oxidation of H<sub>2</sub> over the platinum nanoparticles, 5 vol-% H<sub>2</sub> (99.9%) and 2 vol-% O<sub>2</sub> (99.5%) were added to the platinum aerosol at 25°C. The reaction product H<sub>2</sub>O was detected by FTIR in a concentration of 665 ppm, giving a calculated TOF of 5.36 1/s. Assuming a lower detection limit of 10 ppm H<sub>2</sub>O for the FTIR and average particle parameters in the same range as the one used here, one can derive a lower detectable mass concentration for platinum of 1 ng/cm<sup>3</sup>.

4.1.2. *Methanation of CO over nickel.* After the production of the nickel agglomerates (Figure 3) in the spark discharge generator, the primary particle size was determined to 5 nm and the BET surface of the nickel agglomerates was 132 m<sup>2</sup>/g. The mass concentration  $c_{m,Ni}$  was identified gravimetrically to 30 ng/cm<sup>3</sup> at a stable number concentration in the range of 10<sup>7</sup> nickel agglomerates per cm<sup>3</sup>.

To initiate the reaction, 5 vol-% CO (99.5%) and 25 vol-% H<sub>2</sub> (99.9%) were added to the nickel aerosol. The glass reactor was heated to a reaction temperature of 450°C. The concentration of the reaction product CH<sub>4</sub> measured by FTIR was 0.25 ppm. The TOF under these conditions was calculated to be 1.34 1/s. Thus, the CO methanation over nickel is a slower catalytic reaction than the oxidation of H<sub>2</sub> over platinum. Experiments with other primary particle sizes resulted in a similar production rate of CH<sub>4</sub> in the lower ppm range. These results show that nickel nanoparticles can be detected in the air by direct aerosol catalysis, however only at relatively high concentrations.

4.1.3. *Oxidation of CO over iron oxide (Fe<sub>2</sub>O<sub>3</sub>).* The iron oxide aerosol produced by spark discharge consisted of agglomerates (Figure 3) with a primary particle diameter of 3 nm and a BET surface area of 160 m<sup>2</sup>/g. The aerosol mass concentration  $c_{m,Fe_2O_3}$  immediately after generation was determined to 64 ng/cm<sup>3</sup>; the number concentration of the Fe<sub>2</sub>O<sub>3</sub> agglomerates was approximately 10<sup>7</sup> #/cm<sup>3</sup>.

To initiate catalysis, 2.8 vol-% CO (99.5%) were added to the carrier gas consisting of a 4:1 mixture of Ar and O<sub>2</sub> (99.5%, 1.0 liter/min). The reaction temperature was varied between 100°C and 400°C. These reaction conditions resulted in no reliable detection of the anticipated reaction product CO<sub>2</sub>. Iron oxide does not seem to have sufficient catalytic activity for its detection by aerosol catalysis.



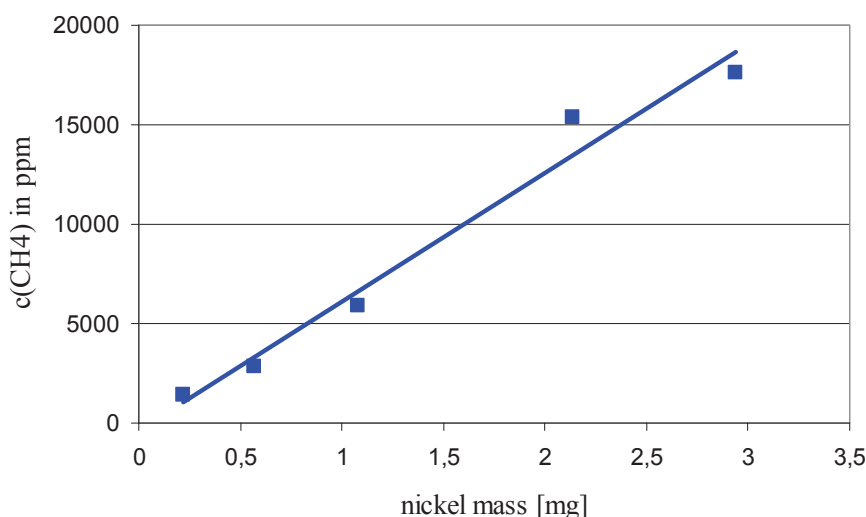
**Figure 3.** TEM images of different ENP produced by spark discharge, from left to right: platinum, nickel, iron oxide (Fe<sub>2</sub>O<sub>3</sub>).



## 4.2. Catalysis on deposited nanoparticles

Experiments were performed with those nanoparticles where the direct catalysis on gasborne particles gave insufficient signals, using the same aerosols and reaction conditions as described before in Chapter 4.1.

4.2.1. *Methanation of CO over nickel.* Nickel nanoparticles were sampled on a filter for a fixed time interval of 1 to 30 minutes at a mass concentration of  $98 \text{ ng/cm}^3$ . The filter afterwards was heated rapidly to  $450^\circ\text{C}$ ; then 5 vol-% CO (99.5%) and 25 vol-%  $\text{H}_2$  (99.9%) were added to initiate the catalytic reaction. The reaction product  $\text{CH}_4$  was detectable by FTIR. Its concentration was related to the mass of the accumulated nickel nanoparticles which was determined by gravimetry. Figure 4 shows the resulting calibration curve for the concentration of  $\text{CH}_4$  vs. the particle mass. At this early stage, each data point represents a single measurement. Nevertheless, it is evident that the concentration of the reaction product  $\text{CH}_4$  increases proportionally to the mass of the nickel nanoparticles. The lower detection limit still remains to be investigated, but can be calculated on the basis of the curve linearity. Currently the lowest studied nickel mass of  $220 \mu\text{g}$  results in 1450 ppm  $\text{CH}_4$ . Assuming a lower detection limit of 10 ppm  $\text{CH}_4$  by FTIR a detection limit of  $2 \mu\text{g}$  nickel nanoparticles can be calculated. This indicates that deposited nickel nanoparticles in the range of a few  $\mu\text{g}$  can be detected by this technique, making it a very fast and near-real time method.



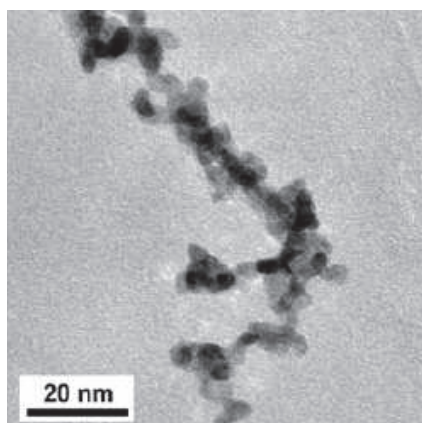
**Figure 4.** Calibration curve for the concentration of  $\text{CH}_4$  against the mass of the nickel nanoparticles during the CO-methanation at  $450^\circ\text{C}$ .

4.2.2. *Oxidation of CO over iron oxide ( $\text{Fe}_2\text{O}_3$ ).* A sampling time of 10 hours at ambient air temperature and a mass concentration of about  $60 \text{ ng/cm}^3$  led to 38.8 mg of iron oxide nanoparticles on the filter. The addition of a 4:1 mixture of Ar and  $\text{O}_2$  (99.5%, 1.0 liter/min) and 2.8 vol-% CO (99.5%) gases at a temperature of  $250^\circ\text{C}$  resulted in 14000 ppm of  $\text{CO}_2$ . A calibration curve similar to Figure 4 as well as the lower detection limit still need to be established. Nevertheless, iron oxide can be detected by the method of catalysis on deposited nanoparticles. Assuming a lower detection limit of 10 ppm  $\text{CO}_2$  by FTIR and curve linearity, this hints that even iron oxide nanoparticles with a mass of  $28 \mu\text{g}$  can be detected via this technique.

4.2.3. *Hydrogenation of ethene over palladium.* The palladium agglomerates (Figure 5) produced by spark discharge and sintered at  $200^\circ\text{C}$  had primary particle diameters in the range of 3 nm. The particle number concentration in the aerosol immediately after the sintering process was in the range

of  $10^7$  agglomerates per  $\text{cm}^3$ ; the corresponding mass concentration  $c_{m,\text{Pd}}$  was determined gravimetrically to  $1.1 \text{ ng/cm}^3$ . Palladium nanoparticles were sampled on a filter for 10 minutes resulting in a mass of  $11 \text{ }\mu\text{g}$ .

To initiate the hydrogenation of ethene, 2 vol-%  $\text{C}_2\text{H}_4$  (99.9%), 2 vol-%  $\text{H}_2$  (99.9%) and 0.05 liter/min  $\text{N}_2$  (99.99%) for dilution were added at  $20^\circ\text{C}$ . The reaction product ethane was detected at a concentration of 4020 ppm. Thus, palladium can be detected easily by this method. The detection limit was not experimentally investigated so far. Calculations result in a preliminary lower detection limit of  $0.03 \text{ }\mu\text{g}$  palladium nanoparticles.



**Figure 5.** TEM image of a platinum agglomerate after sintering at  $200^\circ\text{C}$ .

#### 4.3. Summary of preliminary detection limits

The calculated detection limits for palladium, nickel and iron oxide on the basis of the experimental results of deposited particles are summarized in Table 1. A lower detection limit of 10 ppm for the reaction products by FTIR was assumed. The limit of detection is of course dependent on the device used. For platinum the results of the direct measurement on airborne particles were transferred into a corresponding mass of deposited platinum nanoparticles of  $157 \text{ }\mu\text{g}$  for 665 ppm of the reaction product  $\text{H}_2\text{O}$ . Assuming a detection limit of 10 ppm by FTIR and curve linearity, this results in a lower detection limit of  $2 \text{ }\mu\text{g}$  deposited platinum particles.

**Table 1.** Calculated detection limits for the selected model ENP platinum, nickel, palladium and iron oxide ( $\text{Fe}_2\text{O}_3$ ).

Model reaction	Model catalyst	Detection limit	Sampling time at $1 \text{ mg/m}^3$
Hydrogenation of $\text{C}_2\text{H}_4$	Pd	$0.03 \text{ }\mu\text{g}$	< 3 s
Oxidation of $\text{H}_2$	Pt	$2 \text{ }\mu\text{g}$	< 3 min
Methanation of CO	Ni	$2 \text{ }\mu\text{g}$	< 2 min
Oxidation of CO	$\text{Fe}_2\text{O}_3$	$28 \text{ }\mu\text{g}$	< 30 min



The detection limit for palladium by our method is 2 orders of magnitude lower than that for platinum or nickel which illustrates the known extreme catalytic activity of palladium. The sampling time therefore is in the order of seconds at a concentration of  $1 \text{ mg/m}^3$ . Thus, the described method can be considered a true real-time method for palladium, and a near-real-time method for catalysts with similar activities as nickel or platinum. Iron oxide reacts somewhat more slowly, but then one has to keep in mind that nano-sized iron oxide aerosol particles are not a primary target of concern for ENP, given that it is a very common pollutant in welding and metal treatment fumes, with often unregulated concentrations well above the mg range.

## 5. Summary and Conclusions

A new, substance specific technique for the detection of airborne nanoparticles via their catalytic activity is presented. The method consists of two different experimental approaches. In one case the catalytic activity is determined directly on the airborne particles; in the other, the aerosol is first deposited onto a filter.

In each case, the detection of a specific particle material is based on a specific catalyzed chemical reaction. Four such reactions are investigated here for the materials platinum, nickel, iron oxide ( $\text{Fe}_2\text{O}_3$ ) and palladium. Direct measurements on airborne particles have shown so far that this on-line approach is suitable for very active ENP aerosols in high concentrations, such as platinum or nickel. The detection of platinum and palladium is even possible with a room temperature reaction, whereas the other catalysts require temperatures between about  $250^\circ\text{C}$  and  $450^\circ\text{C}$ . The filter based technique shows a good potential for the detection of less concentrated or less active ENP aerosols based on their catalytic activity. In addition, the filter method can be considered a true real-time method for the detection of palladium and a near-real-time technique for catalysts with similar activities as platinum or nickel.

Tentative detection limits are given on the basis of our preliminary experimental results and assuming a certain sensitivity of the gas analyzers used to measure the concentration of reaction products. It appears possible to detect concentrations in the range of  $1 \text{ ng/cm}^3$  on a time scale of a few seconds for palladium, a time scale of a few minutes for platinum or nickel, and a time scale of about 30 min for iron oxide. An inherent advantage of the method is that its sensitivity increases in proportion to level concern for a given catalyst material.

Future investigations will be directed toward a more accurate definition of detection limits as a function of primary particle size and support material including typical background aerosol particles, as well as a refinement and down-sizing of the test equipment toward a mobile or portable device.

## Acknowledgement

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