Application of catalysis for the specific detection of engineered nanoparticles in workplace air

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The unique properties of engineered nanoparticles (ENP) make them useful in a number of applications and lead to an increasing industrial demand. However, little is known about their interaction with biological systems and the potential risk for workers involved in production or handling of ENP. Another uncertainty arises from the possible adhesion of ENP to the background aerosol of the environment and the resulting disappearance in the size distribution. Therefore it is necessary to determine possible hazards as well as to develop new analytical methods for the characterization and the specific detection of ENP. Catalysis has a great potential with regard to the discrimination of ENP from a background aerosol without catalytic activity.

In the following work the possibility of application of catalysis for the detection of a specific ENP based on its catalytic activity is investigated. Both aerosol catalysis and catalysis on deposited ENP are studied. The method of aerosol catalysis was demonstrated for the methanation of CO over nickel (Weber *et al*., 2006) and the oxidation of H_2 over platinum (Seipenbusch *et al.,* 2001). Aerosol catalysis enables the online measurement of the catalytic activity of nanoparticles. Catalysis on deposited ENP however allows the accumulation of material and thus is potentially better suited for low concentrations or slow catalytic reactions.

As model reaction specific for iron oxide (Fe_2O_3) nanoparticles the oxidation of CO to CO_2 is chosen. In addition the hydrogenation of CO to CH_4 over nickel nanoparticles is studied.

Particle generation and structural modification

The nanoparticles are produced in a spark discharge generator using electrodes of the desired material (iron and nickel of high purity). By using an Ar/O_2-mixture as carrier gas it is possible to oxidize the generated iron particles to iron oxide (Fe_2O_3). Sintering over a defined time enables structural modification.

Aerosol catalysis

After conditioning of the particle structure the educt gases are added to the aerosol before entering the heated reactor initiating the catalytic reaction. The amount of gas phase products of the reaction is monitored online with a Fourier Transformation Infrared Spectrometer (FTIR).

Catalysis on deposited Fe_2O_3 nanoparticles

To increase the catalytically active mass, Fe_2O_3 nanoparticles are sampled on a filter after production in the spark discharge generator. These particles are used as a catalyst in a packed bed reactor. The gas phase products are also detected by FTIR.

Results

Catalytic experiments with the oxidation of CO over aerosol Fe_2O_3 nanoparticles show no reliable detection of the reaction product CO_2. Iron oxide seems to be not catalytically active enough for aerosol catalysis. Using deposited Fe_2O_3 nanoparticles in a packed bed reactor however, sufficient amounts of CO_2 are generated. Thus the ENP Fe_2O_3 can be detected based on its catalytic activity. Calculations of the possible detection limit of deposited Fe_2O_3 yield a minimum mass of 27.7 µg resulting in 10 ppm CO_2. Therefore a sampling time of less than 30 seconds is sufficient at a concentration of 64 mg/m^3.

Investigations concerning the production rate of CH_4 during the methanation of CO over nickel nanoparticles result in the lower ppm-range at concentrations of approximately 10^7 #/cm^3. This also limits the applicability of aerosol catalysis to relatively high ENP concentrations. Calculations concerning the possible detection limit of the ENP nickel show that 4.7 µg of deposited nickel lead to 10 ppm CH_4. Only 10 seconds of sampling time are required at a concentration of 30 mg/m^3.

In summary catalysis enables the specific detection of ENP based on their catalytic activity. The measurement of ENP by aerosol catalysis is limited to very active ENP aerosols in high concentrations. Catalysis on deposited ENP however, requiring a few µg of material, shows a good potential for the specific detection of ENP.

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