

Measurement of chemisorption on metallic nanoparticles using aerosol photoemission spectroscopy

S. Onel and M. Seipenbusch

Institute for Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology, Karlsruhe, 76131, Germany

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Presenting author email: santiago.onel@kit.edu

Chemisorption on metallic nanoparticles is not only a fundamental step in heterogeneous catalysis, but also builds the basis for self-assembled monolayers. We address this topic by working with gas-carried metallic nanoparticles using aerosol photoemission spectroscopy as a highly sensitive analysis tool.

Aerosol photoemission spectroscopy (APES) is a surface sensitive method, which was successfully used in the past showing a correlation between catalytic and photoelectric activity of gas-carried nickel and platinum nanoparticles (Weber et al, 2001). Changes on the particle surface modify the electronic structure, therefore leading to a variation of the photoemission parameters: work function and emission constant. As a result of this, this method shows potential for the study of adsorption on particle surfaces.

In this work we show that APES can be used for the quantitative determination of adsorbates on metallic nanoparticles. This opens up the possibility of measuring size dependent adsorption effects without metal-support interactions or mass transfer limitations due to a support. This online method can be used as well in order to monitor surface functionalization of particles in the gas phase without collecting them or having to perform any other sample preparation step.

Photoemission studies were conducted in an energy range between 5,5 and 6,5 eV, using a deuterium lamp and a monochromator for wavelength selection. The photon energy is just above the work function of metals, but considerably below the ionization energies of the gases used. Work function and emission constant were obtained using the Fowler-Nordheim equation, which describes the photoelectric yield as a function of photon energy near the photothreshold.

Au and Pt nanoparticles were produced in nitrogen 5.0 using a spark discharge generator. The generated particles were mainly aggregates with mean diameters as measured with a scanning mobility particle sizer of 16,6 nm and 18,7 nm, respectively. The primary particle size was determined using TEM being 3,4 nm and 3,8 nm, respectively. The particle number concentration used in both cases was in the order of 10^6 cm^{-3} . The aerosol flow was mixed with the reactant flows: carbon monoxide and 1-hexanethiol. Carbon monoxide 4.7 was dosed using a mass flow controller up to a concentration of 1300 ppm. 1-hexanethiol is liquid at room temperature; consequently, the dosage took place by passing a nitrogen flow through a bubbler filled with 95% 1-hexanethiol. By regulating the nitrogen flow rate and assuming the nitrogen flow is saturated, a maximum concentration of 300 ppm was used.

A positive shift of the work function was observed due to the interaction of CO with Pt. The work function shift increased with increasing CO concentration. The work function shift reached a maximum of 0,23 eV. The data points could be approximated by a Langmuir adsorption isotherm (Figure 1). This can be explained through a growing coverage of the surface with CO and shows consistency with previous results using traditional ultraviolet photoemission spectroscopy for a Pt sheet (Collins et al, 1976). No change in the work function of gold was observed when CO was added, even with higher CO concentrations.

Exposing gold nanoparticles to 1-hexanethiol led to a much larger negative shift of the work function. The effective work function decreased with higher concentration of hexanethiol and reached a saturation value 1,5 eV lower than the work function of the clean surface (5,1 eV). The dependence of the work function on concentration (coverage) was non linear. This behaviour, as well as the maximum value, is in good agreement with theoretical studies (Fragouli et al, 2007)

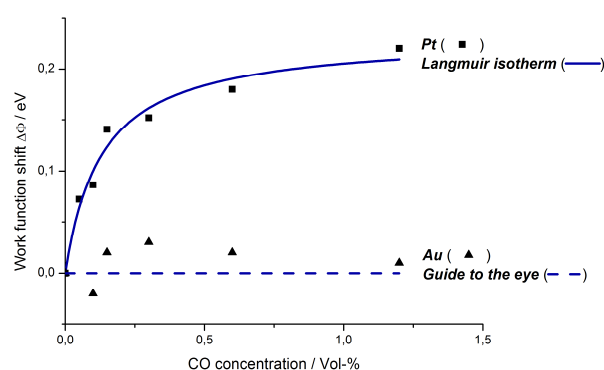


Figure 1. Work function shift as a function of CO concentration

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