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Quantitative analysis of single atom catalysts

Demonstrating the outermost atomic layer sensitivity of LEIS

For many catalysts, the need for efficient use of the valuable metals is leading to smaller particle sizes of the active phase. Ultimately, single metal atoms can act as the catalytically active material. This increases the efficiency, as all metal atoms are exposed at the surface.

Along with the efficiency, the reactivity and selectivity are often improved by using nanoparticle catalysts. This work demonstrates how the Qtac delivers crucial information on such systems.

Determining the fraction of individual atoms on the surface

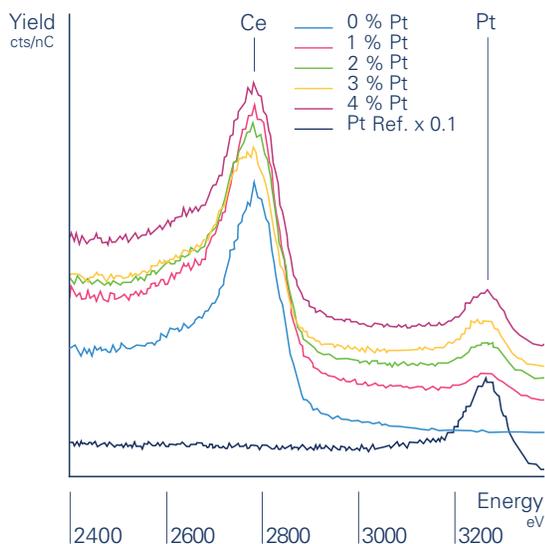


Fig. 1: 5 keV Ne⁺ scattering spectra of the support, the four samples (1 – 4 wt. %), and a Pt reference scaled by 0.1 for comparison. Baseline of the spectra shifted for visibility.

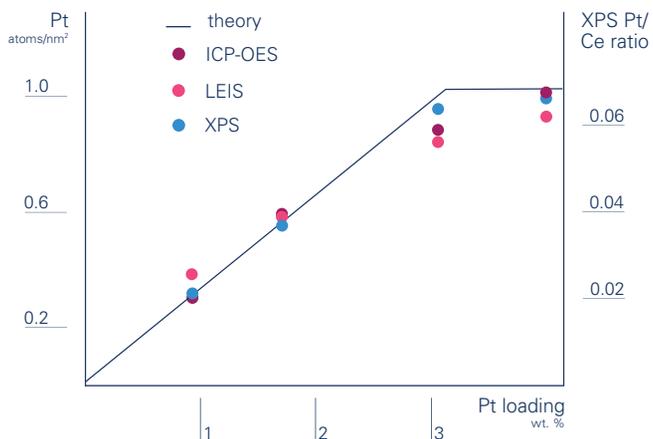


Fig. 2: Pt atoms per surface area as a function of Pt loading as measured with different techniques.

Prof. Datye's group at the University of New Mexico have developed a method to disperse platinum single atoms on an industrial catalyst support. They stabilize the single atoms against sintering at high temperature, allowing much higher loadings than previously possible. In order to verify this finding, LEIS analyses were carried out on materials with 1 - 4 wt. % Pt on CeO₂. Due to the high mass of the Ce atoms in the support, TEM analysis proved difficult as the contrast to the Pt atoms is too low.

In order to measure the number of single Pt atoms on the surface, LEIS analyses using 5 keV Ne⁺ scattering were performed. Ce and Pt surface peaks are well resolved and can be quantified by determining the peak area after background subtraction. (Fig. 1)

During preparation, the samples have been heated at 800 °C in air for 10 h. As small nanoparticles of Pt are not stable under these conditions, only larger particles can co-exist with the individual Pt atoms. These larger particles hardly contribute to the LEIS signal, as the majority of atoms is not at the surface, but inside of the particles.

Based on the number density of Pt in Pt metal the LEIS data can be quantified to yield the number of Pt atoms per nm² for each sample. The second figure shows the number of Pt atoms/nm² determined with various techniques as well as the Pt/Ce ratio determined by XPS.

For the 1 and 2 wt. % samples the LEIS results almost perfectly match the theoretical values assuming full dispersion of the Pt atoms. This is remarkable as the LEIS data is quantified independently, without any assumptions or scaling.

For the samples with 3 and 4 wt. % Pt the LEIS results show 23 % and 31 % less individual Pt atoms than expected, if no clustering would occur. This proves that a large fraction of the Pt is still available as single atoms at these very high loadings.

Here the unique capabilities of LEIS are utilized. Proving this high dispersion with surface analytical techniques can be very challenging, as Pt below the surface or inside of the nanoparticles is detected with all other established techniques. The single atomic layer surface sensitivity of LEIS is crucial for this analysis.