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INVESTIGATION OF Pt/SiO₂ NANOPARTICLES BY SOLUTION AND SINGLE PARTICLE MODE ICP-MS

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Abstract

Pt/SiO₂ nanocomposites (Stöber SiO₂ support particles surface coated with 1.6 nm Pt nanoparticles) were analysed utilizing inductively coupled plasma mass spectrometry (ICP-MS) in the solution and single particle modes. Both analytical approaches were optimized and their performance compared in detail. The single particle ICP-MS approach proposed in this study is a novel approach for the determination of the surface concentration nanoparticles in nanocomposites.

Introduction

In the last decades, the advancement of material science has been fast, and nanotechnology has become one of the most significant and innovative fields of this research direction. The application of nanoparticles (NPs) and nanocomposites in catalysis is particularly desirable due to their specific capabilities. It is important to be noted that the attributes of NPs (size distribution, composition, structure, etc.) can greatly influence the characteristics (selectivity, activity) of the catalytic processes, as well as the lifetime of the catalyst [1]. Therefore, the thorough characterization of NPs is essential in these studies.

Solution mode ICP-MS has already been used for the characterization of the composition of NPs following acid digestion of the particles in recent years. This process is relatively time-consuming and also has the drawback that the determined concentrations (e.g. of surface concentrations) can potentially carry a positive error, as the dissolved analyte content of the original dispersion and the concentration originating from NPs add up. A significant advantage of the novel single particle approach is that it can directly provide information separately about the dissolved analyte content of the dispersion and about the NPs, as well as the size distribution and number concentration of the latter. A small dispersion volume (e.g. a few mL) and as little as 10³ – 10⁵ /mL particle concentration is adequate for the measurement, which requires almost no sample preparation and gives statistically relevant size distribution histograms, which are based on the measurement of tens of thousands of particles. The measurement is also fast, as it takes only about 5-10 minutes per sample. Thus nowadays spICP-MS offers a viable technique for the investigation of individual nano and micro particles of colloidal systems [2], alternative to such widely spread NP characterization methods such as Dynamic Light Scattering (DLS), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM).

The aim of the present study was to develop accurate analytical methods for the determination of the Pt surface concentration in Pt/SiO₂ nanocomposites by ICP-MS both in the solution and single particle modes.

Experimental

Silica support particles, with a typical diameter of 449 nm as determined by TEM, were prepared through a process based on the Stöber method [3]. The 1.6 nm Pt particles used as loading were synthesized by the reduction of PtCl_4 and characterized also by TEM. The Pt nanoparticles were anchored on the surface of SiO_2 support particles by ultrasonic treatment in a nominal concentration of 1 m/m% [4]. TEM images of the Pt/ SiO_2 particles are shown in Fig. 1.

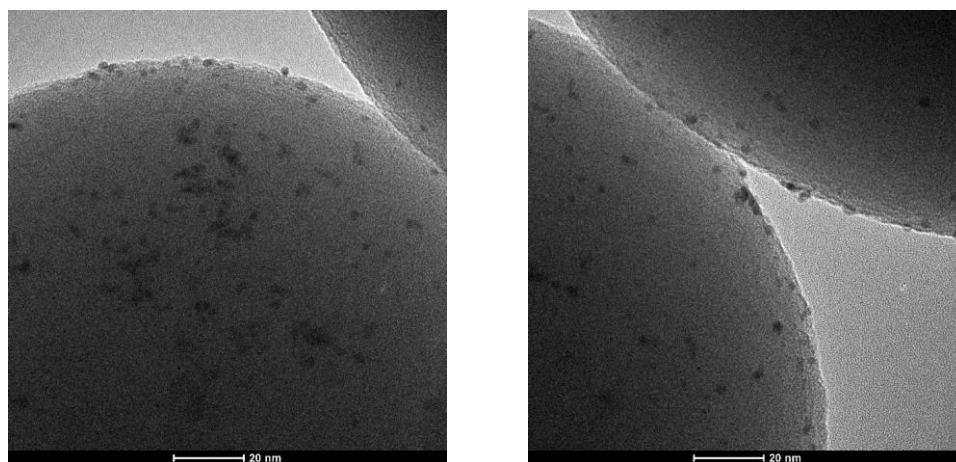


Figure 1. TEM images of the Pt/ SiO_2 nanocomposite particles

An Agilent Technologies 7700 X ICP-MS instrument was used throughout the experiments. Sample introduction was performed by an Agilent I-AS autosampler and a Micro Mist type nebulizer equipped with a Peltier-cooled spray chamber. The sample uptake rate was 400 $\mu\text{L}/\text{min}$. The data acquisition software was used in Time Resolved Analysis (TRA) mode. The integration time of TRA measurement was set to 6 ms. Plasma and interface parameters were optimized prior to the analysis searching for the most resolved and maximum intensity NP signals.

An Agilent Technologies Multi-Element Calibration Standard-3 was used for solution-based calibration. For particle-based calibration, Pt nanosol calibration suspensions were synthesized by the method reported by Bigall et. al. [5], with typical spherical nanoparticle diameters of 21.8 nm, 39.2 nm, 51.0 nm and 81.5 nm.

For solution mode ICP-MS measurements, an acid digestion procedure was optimized for the complete dissolution of the Pt content of the nanocomposite. During the execution of this procedure, we used ultratrace analytical quality nitric acid and hydrochloric acid. Dilution of all solutions and dispersions was carried out by Class I (trace analytical) quality deionized water from a VWR Puranity TU 6 UV/UF device. In order to ensure the homogeneity of the suspensions and to avoid the aggregation of the nano particles, we applied ultrasonic treatment performed by a NEY Ultrasonik 300 instrument.

Results and discussion

Solution Mode ICP-MS measurements were performed by using a mixture of nitric acid and hydrochloric acid (1:3 molar ratio) for digestion. The analysis resulted in 0.281 m/m% Pt content in contrast to the nominal 1%. This indicates that the nominal concentration is a strong

overestimation, which is, of course, not a surprise. That is exactly why the post-synthesis elemental analysis is needed in the first place.

The size of the anchored Pt NPs in the studied nanocomposite presented a challenge for spICP-MS measurements, as the size detection limit of this method for Pt is actually about 18 nm, thus the direct (individual) measurement of particles of 1.6 nm diameter was not possible. The measurement was made possible by the relatively high surface coverage (loading), since the spICP-MS detects the cumulative signal from Pt NPs attached to the silica surface. Hence, the ensemble of Pt NPs on the surface generate a signal which is equivalent to a (virtual) Pt NP larger than the size detection limit.

The first step of spICP-MS measurements to determine the surface concentration of Pt NPs was the particle calibration. As it can be seen in Fig. 2, the calibration plot had a good linearity.

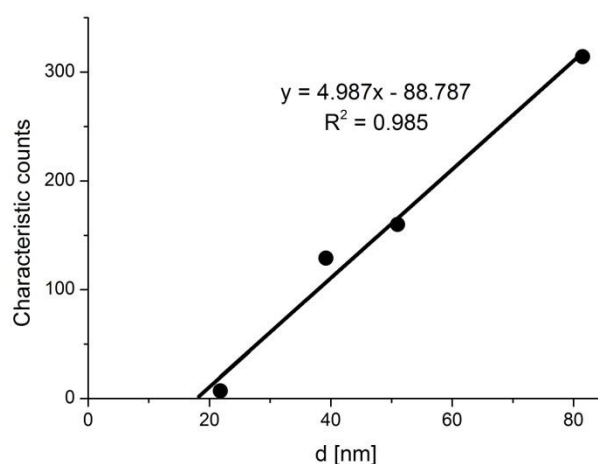


Figure 2. Platinum spICP-MS size calibration curve

The measurement of the nanocomposite samples was performed with an extended 10 ms integration time, and maintaining a low particle concentration in the dispersion, so to ensure an accurate measurement. The histogram of the investigated particles is shown in Fig. 3. As it can be observed, the Pt NP peak is nicely resolved from the background peak. The mode of the peak (the characteristic count) was found to be 11.1, which is equivalent to the signal of a 20.0 nm diameter "hypothetic", spherical Pt particle according to the above calibration curve.

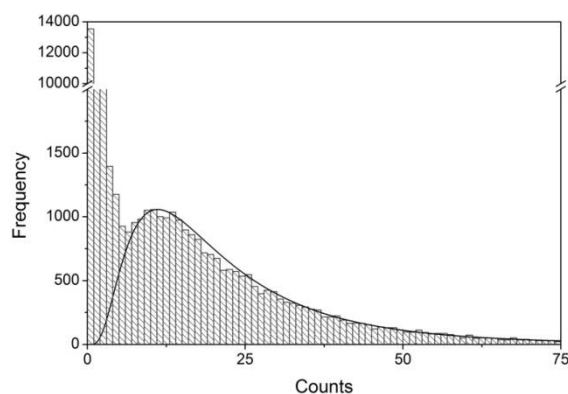


Figure 3. spICP-MS histogram of the nanocomposite particles

(the fitted part originates from the Pt NPs).

Consequently, the Pt surface concentration on a support particle is also equivalent to the mass of this 20.0 nm virtual nanoparticle. This results in a 0.0918 m/m% surface concentration. The result was also confirmed by TEM statistical analysis, during which the surface concentration was determined by the time-consuming counting the Pt NPs on the surface of the silica support in the TEM images. Knowing the size of both the support and the load particles, as well as their specific gravity, the surface concentration could be calculated. This calculation gave a value of 0.0838 m/m%. The good agreement between the spICP-MS and TEM results indicates that spICP-MS can indeed be an accurate and convenient tool in nanocomposite characterization. The fact that both of these results is significantly smaller than the solution mode ICP-MS result indicates that the latter was indeed affected by either the dissolved Pt content (e.g. remnants of precursors) or released Pt NPs from the nanocomposite.

Conclusion

In this study we analysed Stöber SiO₂ support particles surface coated with 1.6 nm Pt nanoparticles utilizing solution and single particle mode ICP-MS. We proved that accurate surface concentration values can be determined by spICP-MS even in cases when the size of the anchored particles are below the size limit of the detection of individual particles. The new technique was less complicated and time-consuming, needed less chemicals and was more accurate than the classical solution-based approach.

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