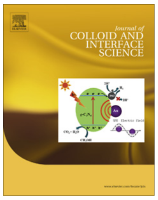
Journal of Colloid and Interface Science 478 (2016) 72–80

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis



Functionalization of small platinum nanoparticles with amines and phosphines: Ligand binding modes and particle stability

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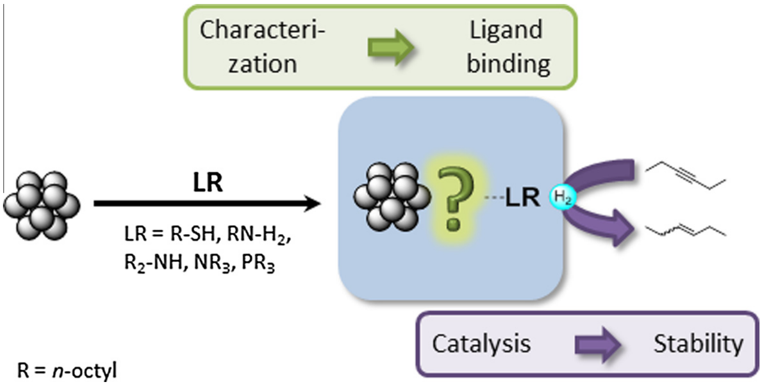
HIGHLIGHTS

- Different functionalization conditions for different ligands are evaluated.
- Functionalization for amines is found to occur only in the presence of hydrogen.
- An alternative way of ligand binding for amines is suggested.
- The binding modes are reflected by the particles' stability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 April 2016
Revised 30 May 2016
Accepted 1 June 2016
Available online 2 June 2016

Keywords:
Nanoparticle
Functionalization
Platinum
Ligand binding
Stability

ABSTRACT

We report the binding mode of amines and phosphines on platinum nanoparticles. Protective ligands comprising different functional groups are systematically studied for the elucidation of ligand binding at different functionalization conditions. From the functionalization conditions it is concluded that the binding of amines to the nanoparticles occurs *via* the formation of a Pt—H—N moiety or electrostatic interaction, which is supported by spectroscopic evidences. In particular from complex chemistry such a binding mode is surprising, as amines are expected to bind *via* their electron pair to the metal. Similar results from functionalization are observed for phosphine-protected nanoparticles, which suggest similar binding modes in these systems. In contrast to the strong covalent bond of the protection with thiols, considerable weakly binding systems result. The characteristics of the binding mode are reflected by the stability of the colloids and their catalytic properties. In the selective hydrogenation of 3-hexyne to 3-hexene thiolate-stabilized Pt particles are highly stable, but exhibit the lowest activity. On the other hand, amine- and phosphine-capped platinum nanoparticles show a significantly higher activity, but rapidly agglomerate.

1. Introduction

Metal nanoparticles are applied in various fields of research, such as chemistry and biology [1–4]. Broad areas of application are for example sensing, material science and catalysis [5,6]. The

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http://dx.doi.org/10.1016/j.jcis.2016.06.003

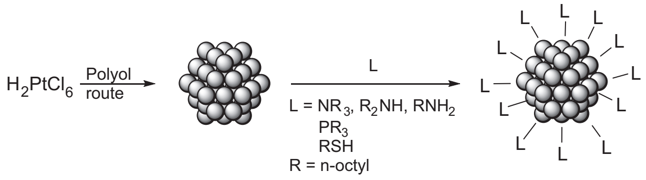
interest in the nanoparticles arises from their unique properties, as e.g., their high ratio of surface-to-bulk atoms. Very small particles, commonly called clusters, even exhibit unexpected optical and catalytic properties, which do not scale with their size. For example, for the CO oxidation reaction it is found that platinum (Pt) clusters up to some tens of atoms show an atom-by-atom dependent reactivity [7]. The nanoparticles and clusters can be used either as heterogeneous systems by their deposition onto a support material or homogeneously as colloids. In both applications fast ripening processes may be observed, which strongly reduce the stability of the particles [8].

One way to increase the stability of the nanoparticles is their protection by an organic ligand shell. These organic molecules bind to the metal particles and avoid agglomeration so that their sizes are preserved. The ligands can further be used to tune the physical and chemical properties of the particles as their solubility or the absorption of light [9,10].

With such an approach also the selectivity of certain catalytic reactions can be altered [11–13]. In particular selective hydrogenation reactions, such as the reaction of alkynes to alkenes, are exceedingly studied in several fields in chemistry [14]. A prominent catalyst for this reaction is the Lindlar type catalyst [15]. Its working principle is based on the partial poisoning of the catalyst surface [16]. The same concept is already applied in research for colloidal metal nanoparticles, where different metals and ligands are used for the alkyne semihydrogenation [17–20]. However, in all these studies the role of the ligand is solely studied in dependence of its concentration, but more detailed investigations on ligand binding have not been carried out. In this respect, a first attempt was undertaken in a recent study to systematically investigate the role of the capping ligand on the selective hydrogenation of alkynes to alkenes [11]. While DFT calculations were preformed to support the drawn conclusions, a more detailed characterization by spectroscopy of the catalysts and their stability was not given. However, the binding strength and mode of the ligand is expected to strongly influence the catalytic behaviour and is even observed in the previously mentioned study [11]. Thus, elucidating ligand binding is crucial for a rational design of ligand protected particles for various applications, as for example in catalysis [21].

In case of thiols the binding of the ligand to Pt nanoparticles is very well explored. The disappearance of the S—H stretching vibration, which lies in a considerably "silent" wavelength region in the IR spectrum, indicates that a rather strong covalent Pt—S bond is formed [22]. However, already for amines the situation is less clear. In analogy to complex chemistry, it is generally believed that the ligand binds *via* the free electron pair of nitrogen to the cluster surface. Such structures are for example supported by DFT calculations on Pt_{55} clusters [23]. For the phosphine the anchoring to the cluster is expected to occur in a similar way *via* the free electron pair of the phosphorous atom [24,25].

For the protection of Pt nanoparticles in a similar size regime, we have selected five different ligands, which are similar in their structure but differ by their functional group. Amine-, phosphine- and thiolate-stabilized platinum nanoparticles (Scheme 1) were obtained by varying the functionalization conditions and thoroughly characterized. In a subsequent step the samples were applied as homogeneous catalysts for the selective hydrogenation of 3-hexyne to 3-hexene. In addition, the degree of substitution and its implication on the catalysts' properties were studied for the amines. In the following, we elucidate the mode of ligand binding and, based on these findings, supply a detailed interpretation for the catalytic properties and the stability of ligand protected clusters in general.



Scheme 1. Synthesis route for nanoparticle formation and stabilization.

2. Experimental section

2.1. Materials and methods

$H_2PtCl_6\cdot 6H_2O$ was purchased from Sigma Aldrich and used without further purification. For all reactions in hydrogen atmosphere, hydrogen 6.0 from Westfalen AG was used. All ligands were purchased from VWR International as "per analysis" grade. The phosphine was stored under an Ar atmosphere. All ligands were used as received. All solvents were distilled prior to being used.

IR absorption spectra were recorded using a Thermo Scientific Nicolet 380 FTIR spectroscope with a resolution of 4 cm^{-1} and 32 scans per measurement. All ligands and the corresponding stabilized particles were measured in transmission in a KBr liquid cell with CCl_4 as solvent.

^{1}H NMR spectra were recorded on a Bruker AVANCE III 400 instrument. For variable temperature (VT) NMR experiments, a Bruker DRX 400 was used. ^{31}P magic-angle-spinning (MAS) NMR solid state spectra were recorded on a Bruker Avance 300. Chemical shifts are reported in ppm relative to the signal of tetramethylsilane using the residual signals of $CDCl_3$ at 7.62 ppm and 1.73 ppm for THF-d_8 for the ^{1}H NMR spectra, respectively. The resonance signal of solid ammonium dihydrogen phosphate was used as an external standard for all ^{31}P MAS NMR spectra at 1.1 ppm with respect to phosphoric acid.

All samples (about 8 mg) were measured under argon atmosphere in a TG/DAT Q5000 IR device (TA Instruments, Inc.). A heat rate of 10 °C/min was applied to the samples up to a maximum of 1200 °C for the TGA analysis.

A JEM 2012 transmission electron microscope (JEOL) was employed to record the images of the platinum nanoparticles with an acceleration voltage of 120 kV. A drop of the colloid sample was applied to a carbon-coated copper grid and allowed to dry in air. Nanoparticle sizes were determined from the diameter of 200 random particles by constructing of size-dependent histogram (see Supporting Information).

Analysis of all samples by gas chromatography was conducted at a Hewlett-Packard – HP 6890 Series GC System (Agilent Technologies Inc.) with an Astec® CHIRALDEX G-TA column and FID. The temperature gradient was started at 40 °C, which was held for 8 min. Then, heating of 20 °C/min up to 200 °C was applied followed by a hold at this temperature for 6 min. A cooling phase of 40 °C/min down to 150 °C finished the measurement.

2.2. Synthesis

The synthesis of "unprotected" soluble platinum nanoparticles was performed in analogy to the method of Wang et al. [26]. In a typical experiment 0.25 g $H_2PtCl_6\cdot 6H_2O$ (0.48 mmol, $\geqslant$37.50% metal, Sigma-Aldrich) was placed under argon in a 250 mL-Schlenk flask and 25 mL ethylene glycol (99%, Alfa Aesar) were added. A solution of NaOH (99%, Grüssing) in ethylene glycol (25 mL, 1.0 M) was added and stirred vigorously to obtain a homogeneous mixture. The solution was heated to reflux at 150 °C for 1.5 h (500 rpm). The clear yellow solution turned black after