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1-Naphthylamine functionalized Pt nanoparticles: Electrochemical activity and redox chemistry occurring on one surface

Eva Morsbach[1], Markus Nesselberger[2], Jonas Warneke[1], Philipp Harz[1], Matthias Arenz[2], Marcus Bäumer[1], Sebastian Kunz[1]*

[1] IAPC (Institute of Applied and Physical Chemistry), University of Bremen, Leobener Str. NW2, 28359 Bremen, Germany; [2] Nano-Science Center, Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen, Denmark

* Corresponding Author:

Dr. Sebastian Kunz

University of Bremen

Institute for Applied and Physical Chemistry (IAPC)

D-28359 Bremen

Tel: +49-421-218 63187

eMail: SebKunz@uni-bremen.de

ABSTRACT

We present the preparation and electrochemical application of Pt nanoparticles (Pt NPs) functionalized with 1-naphthylamine. Under electrochemical conditions, Pt surface bound 1-naphthylamine (NA) can be reversibly switched (oxidized and reduced), while simultaneously electrocatalytic reactions (e.g. CO oxidation) can proceed on the Pt surface. While the redox activity of the ligand is established immediately after functionalization, the functionalized NPs have to be stored as a colloidal dispersion in tetrahydrofuran (THF) prior to deposition onto the support material in order to induce their catalytic activity. We interpret this catalytic activation due to partial desorption of ligands from the particle surface induced by storing the particles in THF. However, the experimental results do not indicate a loss of ligands from the ligand shell, but evidence that the ligands form oligomers when kept as colloids in THF. As a result the catalytic surface becomes partially available while the redox activity of the ligands is maintained.

1. Introduction

The presence of organic ligands (capping agents) on nanoparticle (NP) catalysts has often been regarded as a hindrance for applications in heterogeneous catalysis, because they bind to the surface, leading to partial blocking of active sites.[1, 2] For ligand-functionalized NP catalysts the accessibility of surface atoms is determined by the steric demand and the coverage of the ligand.[3, 4] At a full monolayer of ligands (denoted to as ligand coverage = 1) all surface atoms are blocked and no catalytically active surface area can be determined.[4, 5] As a consequence, the application of colloidal NPs for the preparation of model catalysts is most often preceded by removal of the ligands.[1, 6, 7]

In the last years, several studies have demonstrated that ligands attached to metal NPs are able to modify the NP's geometric and electronic surface properties.[5, 8, 9] Via the functionalization the selectivity of heterogeneous liquid-phase and gas-phase catalysts can be enhanced and in some cases even activity.[9-13] Besides surface modifications, ligands can also interact directly with adsorbed

reactants, which enables the control of chemo- and stereoselectivity.[14, 15] These examples demonstrate that ligands may not merely serve as spectator species but are suitable to participate in catalytic reactions.

Apart from investigations in heterogeneous liquid and gas-phase catalysis, the use of ligand-functionalized NPs in electrocatalysis is recently gaining increasing interest. To the best of our knowledge so far ligands have only been used to modify the geometric[11, 16] and electronic[17, 18] surface properties, with the ligand backbone acting as a passive spectator. The question thus arises if one can utilize ligands which by themselves are electrochemically active. In this way, one could obtain bifunctional materials, as ligand and particle may both be electrochemically active or even achieve synergistic effects between the metal and the ligand. In order to address this question the presented work focuses on Pt NPs functionalized with 1-naphthylamine (NA), an aromatic molecule that exhibits well-characterized redox properties[19-21] and allows for proper binding to the particle surface. The functionalized NPs were characterized in detail and their electrochemical characteristics were investigated, revealing that the properties of both ligand and particle can be combined within one material.

2. Experimental Section

2.1 Synthesis of "unprotected" Platinum nanoparticles

The nanoparticle colloids were synthesized following a polyol route reported in literature[22] and described in more detail before[4]. Briefly, the metal precursor $H_2PtCl_6 \cdot 6H_2O$ (100 mg, ChemPur, 40 wt% Pt) was dissolved in 5 mL of ethylene glycol (EG, Sigma-Aldrich Germany, ≥ 99.5%) to result in a metal concentration of 41 mM. The precursor solution was mixed under vigorous stirring with 5 mL of a 0.4 M NaOH/EG (sodium hydroxide, Fluka, >97%) solution. The yellow reaction mixture was then heated to 160 °C within 10 minutes and kept at this reaction temperature for 3 h. Within 5 minutes the yellow solution turned black indicating the formation of Pt NPs.

2.2 Functionalization of Pt NPs with 1-Naphthylamine (NA-Pt NPs)

In order to ensure the maximum ligand coverage, the functionalization of Pt NPs with 1-naphthylamine is performed in an excess of ligand. A Pt NP dispersion sample of 0.5 mL was diluted with 4.5 mL of fresh ethylene glycol. 15 mg of 1-naphthylamine (NA; Merck, > 99.1 %) was dissolved in 5 mL of chloroform ($CHCl_3$, VWR, 99.1 %) resulting in a concentration of 0.02 mol L^{-1} corresponding to a 10-fold excess of ligand molecules compared to the platinum concentration. The ligand solution and NP dispersion was mixed and stirred vigorously over night to ensure proper mixing of both phases. Thereby ligands bind to the NPs, accompanied by a phase transfer of the functionalized NPs into the unpolar phase. After 1 h of resting two distinct phases were formed. The black color of the chloroform phase indicated successful NP functionalization and phase transfer. The EG phase was discarded while the dispersion of functionalized NPs was concentrated by solvent evaporation. Subsequently, the particles were precipitated by adding acetone (VWR, p.a.) by changing the solvent polarity. After washing the precipitate with acetone to remove residual, non-binding ligands, the NPs were dispersed in 1 mL of tetrahydrofuran (THF, Riedel- de Haën, ≥ 99.9 %) for all further steps which gives a stable dispersion of functionalized NPs.

2.3. Storage induced catalytic activation of NA-Pt NPs

The isolated and washed NA-Pt NPs were stored as dispersed particles in THF (see 2.2 for preparation) under ambient conditions for several days. Storage should lead to partial ligand desorption until thermal equilibrium is achieved which is mainly determined by the heat of adsorption. Following this idea the NA-functionalized Pt NP dispersion was left at ambient conditions for 5 and 10 days in order to equilibrate the number of free surface sites. These samples, denoted as “catalytically activated NA-Pt NPs”, were then further applied in cyclic voltammetry and characterized in the same way as the fresh NA-Pt samples (see 2.4 - 2.10).

2.4 Deposition of NA-Pt NPs on carbon support

Deposition of freshly prepared and catalytically activated NA-Pt NPs were performed by the same routine. NA-Pt NPs were deposited from the THF dispersion onto carbon support by mixing 342 µL of the NP dispersion with 1.60 mg of high surface area carbon (Vulcan XC72R, Cabot Corporation) to give a nominal Pt loading of 30 wt%. Then solvent evaporation was achieved at ambient conditions while sonicating the dispersion to achieve an even distribution of the particles on the support surface.[23]

2.5 Cyclic voltammetry and CO stripping

Electrochemical measurements were performed with a three-compartment electrochemical Teflon cell [24], using a multi-electrode setup[25] with eight glassy carbon (GC) tips (8x5 mm diameter, 0.196 cm^2 geometrical surface area) as working electrodes (WE) and a computer controlled potentiostat. The counter (auxiliary) electrode was a Pt wire, the reference electrode a saturated calomel electrode (SCE). The reference electrode was placed in an additional membrane (Nafion®) separated compartment in order to avoid the diffusion of Cl^- ions into the main compartment. [26] All solutions were prepared in Millipore® H_2O (>18.3 MΩ cm, TOC < 5 ppb).

Prior to the measurements the GC working multi-electrode was polished to mirror finish using alumina oxide paste 0.3 and 0.05 µm (Buelher-Met, deagglomerated α-alumina and γ-alumina, respectively), and cleaned ultrasonically in ultrapure H_2O and cc. 70% $HClO_4$. To achieve a homogeneous sample coating on the electrode tip the NA-Pt NP loaded carbon was dispersed in 2 mL of Millipore® water and then 11.5 µL of the dispersion was deposited onto the electrode tip. Due to the difficulty of achieving homogeneous catalyst dispersions, the electrode loading was found to vary for the different samples, which led to quite high deviations of the measured electrochemical surface areas. After preparation the samples were dried in a nitrogen gas stream.

All electrochemical experiments were performed in 0.1 M $HClO_4$ (Merck, suprapure) solution at ambient temperature. Prior to the measurements the electrolyte was de-aerated by purging with Ar

gas (4.8; Air Liquide), and the measurements were started with cleaning the catalyst by potential cycles between -0.30 and 0.85 V_{SCE} at a scan rate of 100 $mV \cdot s^{-1}$. The solution resistance between the working electrode and the Luggin capillary was digitally compensated, resulting in an effective solution resistance of less than 5 Ω in each experiment.

After adsorbing CO at a potential of -0.30 V_{SCE} until saturation coverage was reached, CO stripping curves were recorded in CO-free Ar saturated solution. Concomitantly the electrolyte was purged at least for 10 min with Ar and thereafter CO electrochemically oxidized by cycling the potential between -0.30 and 1.00 V_{SCE} with a scan rate of 0.10 Vs^{-1}.

2.6 Transmission FT-IR Spectroscopy

"Unprotected" Pt NPs were isolated from the reaction mixture by precipitation and re-dispersion as described previously.[4] For preparation, dispersing, and storage of NA-Pt NPs see 2.1-2.3. For IR spectroscopic investigations "unprotected" and NA-functionalized Pt NPs stored for different periods were deposited onto a Si substrate by drop-casting of the corresponding dispersion. The samples were kept at ambient conditions until solvent evaporation was completed. Measurements were carried at a evacuable Vertex 80v Bruker spectrometer at a resolution of 4 cm^{-1} and collecting 100 scans. Prior to each sample measurement, background scans of the clean Si wafer were recorded.

2.7 Transmission electron microscopy studies

Transmission electron microscopy (TEM) images were recorded with a Tecnai F20 S-TWIN microscope (FEI) and a Jeol JEM-2100F, both operated at 200 kV. The "unprotected" Pt NP and NA-Pt NP dispersions (see 2.1-2.4) were diluted with acetone and THF, respectively, prior to deposition. Samples of "unprotected" Pt NPs and NA-Pt NPs were prepared by drop-casting the corresponding colloid onto a carbon-coated copper grid (Quantifoil®, Cu 200 mesh). The samples were dried at ambient conditions until the solvent was completely evaporated. The average particle size for each

sample was determined using the open source software ImageJ and measuring at least 200 individual NPs.

2.8 Determination of Elemental Composition

For elemental analysis (EA) and atomic absorption spectroscopy (AAS) of freshly synthesized NA-Pt NPs (as described in 2.2) and samples stored for 5 and 10 days (see 2.3) the solvent was removed by evaporation at ambient conditions. For the stored samples an additional washing step had to be performed to ensure that ligands that have desorbed are removed from the samples prior to analytic measurement. Therefore the samples were rinsed with acetone and then again dried under vacuum until no further mass decrease was detected. C, H and N contents were determined using an elemental analyzer (Euro EA) with chromatographic separation and a TCD. To measure the Pt concentration, the samples were digested in freshly prepared aqua regia and a fast sequential atomic absorption spectrometer (Varian AA 280 FS) was used.

2.9. NMR Spectroscopy

The NA-Pt NP samples were prepared as described in 2.2. In order to remove non-deuterated solvent residues, the functionalized NPs were dispersed in 1 mL of d_8- THF (deutero, 99.5%) and the solvent was removed at a rotational evaporator. Subsequently, the sample was dispersed in fresh d_8-THF and was transferred to a NMR tube. ^{1}H NMR spectra were recorded on a *Bruker AVANCE NB-360* (8.46 T, 360 MHz). Offset frequency and spectral width were adapted to the chemical shift being investigated, all other parameters were used with default settings.

2.10. Mass spectrometry

Electrospray Ionization mass spectrometry (ESI-MS) measurements were performed on a *Bruker Esquire-LC* ion trap mass spectrometer. First, the pure ligand dissolved in methanol (HiPerSolv-

CHROMANORM, HPLC-Gradient-Grade) was measured. Subsequently, 30µL of the NP dispersion in THF were dispersed in 500µL methanol. After precipitation of the particles at the bottom of the tube, the solution was injected into the mass spectrometer via a syringe pump at a flow rate of 3 µL/min. Spectra were recorded in the positive ion mode for one minute and averaged.

3. Results and Discussion

Electron transfer reactions can be investigated by cyclic voltammetry (CV), as each charge transfer process leads to a corresponding current in the cyclic voltammogram.[27] Thereby, it must be distinguished between irreversible and reversible redox reactions. The latter is indicated by an oxidation and reduction peak in the anodic and cathodic scan, respectively. One example is the adsorption and desorption of hydrogen on Pt (U < 0 mV), which is shown for pure Pt NPs in Figure 1a (grey graph). An irreversible reaction is observed if either the oxidation peak or the reduction peak is absent. An example is the electrocatalytic oxidation of adsorbed carbon monoxide (CO) with the help of co-adsorbed O-containing species ("CO stripping") on Pt surface sites which can be visualized by the characteristic peak of the CO stripping cycle (see Figure 1a, black line). In addition, the integrated peak serves as a measure for the electrochemically active surface area (ECSA).[28]

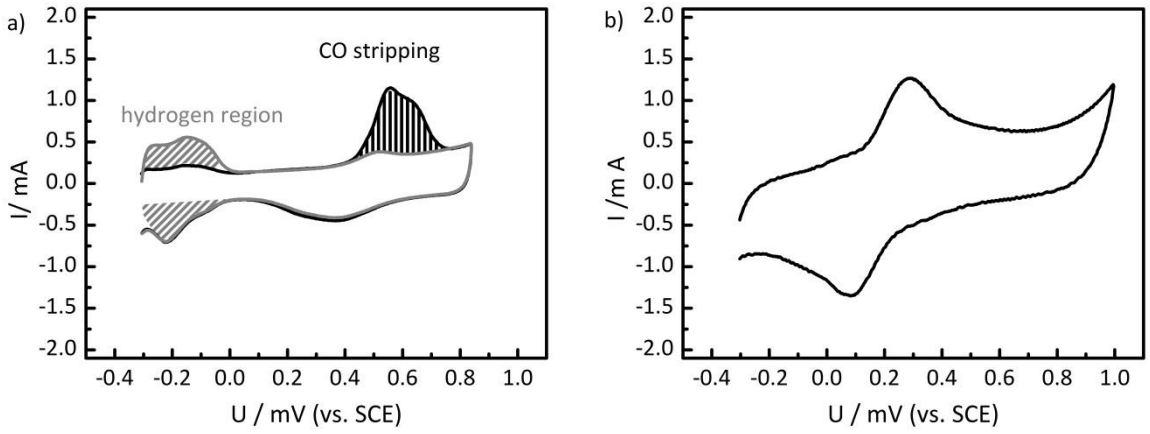

Figure 1: a) Polarization curves of the CO stripping (black) and background cycle (gray) of pure Pt NPs supported on Vulcan carbon. b) Cyclic voltammogram of fresh NA-Pt NPs supported on Vulcan carbon. The response from an active redox couple can be attributed to the ligand redox reaction, while no ligand-free Pt sites related features are visible.

In contrast to pure Pt NPs (Figure 1a), the CV of freshly prepared NA-functionalized Pt NPs supported on carbon (Figure 1b) does not reveal the characteristic features of Pt NPs. The hydrogen under potential deposition (H_{UPD}, ca. 0 → -0.3 V in the backward scan), which often is used to quantify the free Pt surface area, is suppressed. In addition, no CO oxidation was detected during a CO stripping cycle, so it can be assumed that the complete Pt surface is blocked and no ECSA can be determined for fresh NA-Pt NP samples. Instead, a response from an active redox couple (oxidation around 0.3 V, reduction around 0.1 V) is obtained. With respect to the electrochemical oxidation and reduction properties of poly-naphthylamine, we relate these peaks to the reversible oxidation and reduction of the NA ligand.[20, 29, 30] The presence of these redox peaks thus indicates that the redox properties of naphthylamine can be maintained upon functionalization of Pt NPs with NA. Therefore, the charge will be transferred between the aromatic system and Pt NPs via the orbitals of the amine head group.[31] With respect to the known redox properties of aromatics, we assume that a radical cation is formed during the electrochemical oxidation where the charge is delocalized over the aromatic system.[32]

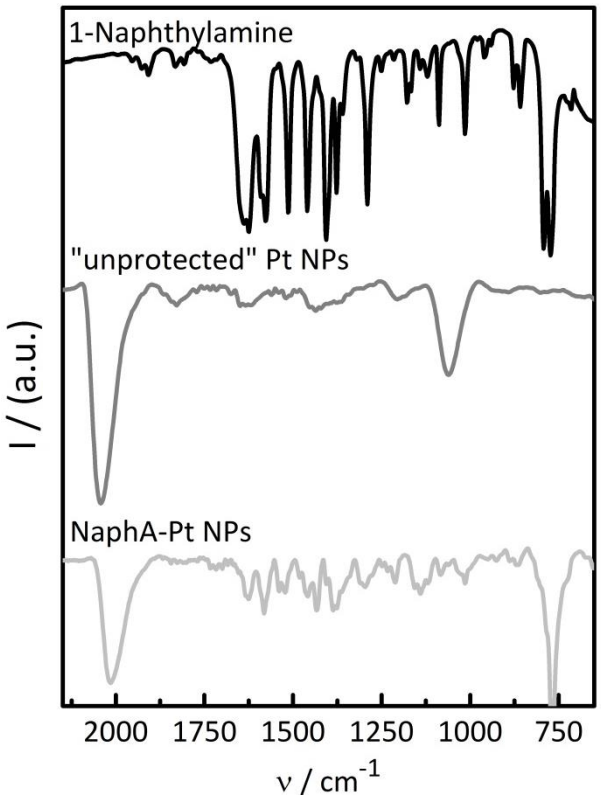

Figure 2: Functionalization of Pt NPs with 1-naphthylamine, characterized by transmission IR spectroscopy. The black spectrum is the pure ligand. Unfunctionalized Pt NPs are shown in the middle (dark grey spectrum). The functionalized NA-Pt NPs are presented by the light grey spectrum.

In order to demonstrate that naphthylamine is indeed bound to the particle surface, IR spectroscopy was applied to investigate the ligand shell (see Figure 2). The spectrum of NA-Pt contains the diagnostic vibrations of naphthylamine, indicating that the particle bound ligand is intact. Ligand-free surface sites on functionalized Pt NPs prepared by the applied route are indicated by the presence of CO adsorbed on Pt.[4] Although no ECSA could be determined for fresh NA-Pt by CO stripping experiments, the presence of a characteristic Pt-CO band at 2015 cm^{-1} in the NA-Pt spectrum reveals the presence of ligand-free surface sites. The vibration at 2015 cm^{-1} is close to the singleton frequency reported for CO on such systems.[5] We thus conclude that the CO molecules adsorbed on NA-Pt NPs are not adjacent to other CO molecules as this would cause dipole-dipole coupling induced shifts.[33] In contrast, the CO molecules are isolated from each other due to the presence of the sterically demanding ligands which can be assumed to be evenly distributed over the particle surface.[34]

The isolation of free Pt sites by the ligands is in agreement with the absence of any catalytic CO oxidation activity. For the electrochemical oxidation of CO on Pt, co-adsorption of CO and the reactive oxygenate is prerequisite, similar as to heterogeneous gas-phase reactions. [28, 35] The reactive oxygen species is generated by dissociation of H_2O on a free surface site to form adsorbed OH, while the remaining proton is released into the solvent.[36] If adjacent free surface atoms become isolated by the presence of non-reactive adatoms or ligands, reactants will adsorb on spatially separated sites, and, as a result, the oxidation of CO becomes suppressed as the two reactants cannot "meet". For example, Selenium atoms (coverage > 0.33 monolayer), which do not alter the electronic properties of Pt, form an evenly distributed adatom layer on a Pt electrode that inhibits CO oxidation and hydrogen adsorption.[37] Similar to a Se adatom layer, a dense coverage of ligands may hamper the co-adsorption of OH and CO on adjacent Pt surface sites, which is required for the reaction to proceed.[28] As a result, the CO stripping on fresh NA-Pt NPs is suppressed although IR spectroscopy indicates the presence of ligand-free surface atoms by Pt bound CO.[4]

With respect to the bond strength of amines on Pt ,[38] it can be assumed that in a colloidal dispersion of functionalized NPs the ligands are in a dynamic adsorption-desorption equilibrium.[39] Therefore, NP functionalization with amines is performed in an excess of ligands to ensure high ligand coverage. If amine functionalized Pt NP dispersions are stored for several days, usually an excess of ligands is added to the dispersion to maintain this high ligand coverage, which as a consequence inhibits coalescence of particles. However, for the electrocatalytic oxidation of CO adjacent ligand-free surface sites are required, as discussed above.[28] We thus tried to catalytically activate NA-functionalized NPs by storing the cleaned particles in THF in the absence of any dissolved ligands to achieve partial ligand desorption (see 2.3). From TEM characterization performed with samples that were stored for 5 and 10 days it can be concluded that particle coalescence does not occur within this time period (see Supplementary Information, Figure S1). CV and CO stripping experiments performed with NA-Pt NPs that were left for 5 days in THF are shown in Figure 3.

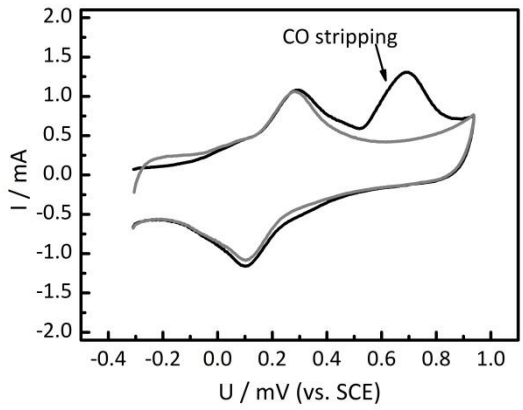

Figure 3: CV and CO stripping experiments of catalytically activated NA-Pt NPs. The reversible ligand redox peak is maintained, while CO stripping peak arises. The black curve corresponds to the CO stripping cycle, while the grey graph shows the background cycle (potential cycle after CO oxidation).

While the CVs of catalytically activated and fresh NA-Pt NPs are identical, significant changes are observed in the CO stripping cycle. In the CO stripping experiment of the catalytically activated NA-Pt NPs, the ligand redox peaks remain identical to the CV, while a second peak, attributed to CO oxidation on Pt,[28] arises. With regard to the above discussion we conclude that adjacent free Pt surface atoms are formed by storing the sample that then allow for the oxidation of CO. An increasing ratio of catalytically active Pt sites to the ligand redox peak was obtained for proceeding activation periods (see Table 1), demonstrating that NA-Pt NPs indeed become catalytically activated by storage as colloids in THF while the redox properties of the ligand are maintained.

Table 1: Ratio of CO stripping to redox reaction of NA-Pt for different activation periods.

	CO-stripp : Redox
day 1	0
day 5	1.2 ± 0.3
day 10	2.6 ± 0.4

In order to prepare supported, ligand-functionalized NPs that do not show ligand desorption when applied in liquid media, it is necessary that the ligand is insoluble in the reaction medium.[15]

Naphthylamine is insoluble in water, even under acidic conditions, and should thus not desorb from the NP surface during the potential cycles. In order to demonstrate that the ligand related peaks in the CV indeed originate from Pt bound ligands, we tried to dissolve the same amount of NA as present in a NA-Pt NP sample in fresh electrolyte and expose it to potential cycles. Due to the insolubility of NA, no redox peak can be observed. Disappearance of the ligand shell via spillover onto the support can furthermore be excluded as the H_{UPD} remains suppressed on the activated NA-Pt NPs. It is thus concluded that under electrocatalytic conditions the chemical properties of the ligand shell of the functionalized Pt NPs is maintained.

As mentioned above, our hypothesis for the catalytic activation of the samples via storage as colloids is that storing the functionalized particles in the absence of an excess of ligands leads to partial ligand desorption. To further characterize the functionalized Pt NPs and to explore the activation mechanism additional measurements were performed on as-prepared and activated NA-Pt NPs.

Table 2: Experimental and theoretical elemental ratios of N and Pt surface atoms for fresh and activated NA-Pt NPs. The elemental ratios are normalized to Pt surface atoms. The experimental values were determined from elemental analysis and atomic absorption spectroscopy.

	$n_{(theo)}$	$n_{(exp)}$ „fresh“	$n_{(exp)}$ 5th day	$n_{(exp)}$ 10th day
N	1.0	0.9	1.0	1.1
Pt surface atoms	1.0	1.0	0.9- 1.0	1.0

EA/AAS of fresh and activated NA-Pt NPs were performed to investigate if significant changes of the ligand coverage occur upon storage as colloids. The theoretical values for full ligand coverage and the experimental values are presented in Table 2. A 1 : 1 ratio of nitrogen (N) to Pt surface atoms corresponds to a full monolayer of ligands on the Pt NPs. For the fresh sample, the 0.9 : 1.0 ratio between N and Pt indicates the presence of an almost complete monolayer of naphthylamine on the NPs (1 ligand per surface atom). The N : Pt ratio does not change significantly as the storage period of the colloids in THF is varied, so that the results obtained by EA and AAS do not indicate any ligand

loss for the catalytically activated samples. Instead, a different mechanism must account for the activation of NA-Pt NPs.

In order to probe suitable changes in the ligand shell that may allow for drawing conclusions regarding the activation mechanism, ^{1}H-NMR spectroscopy was performed. First a spectrum of fresh NA-Pt NPs dispersed in deuterated THF was recorded. This sample was then stored, as done for the catalytic activation, and spectra were taken at different stages of catalytic activation (after 3, 7, and 14 days). No significant changes were observed in the spectra (see Figure 4).

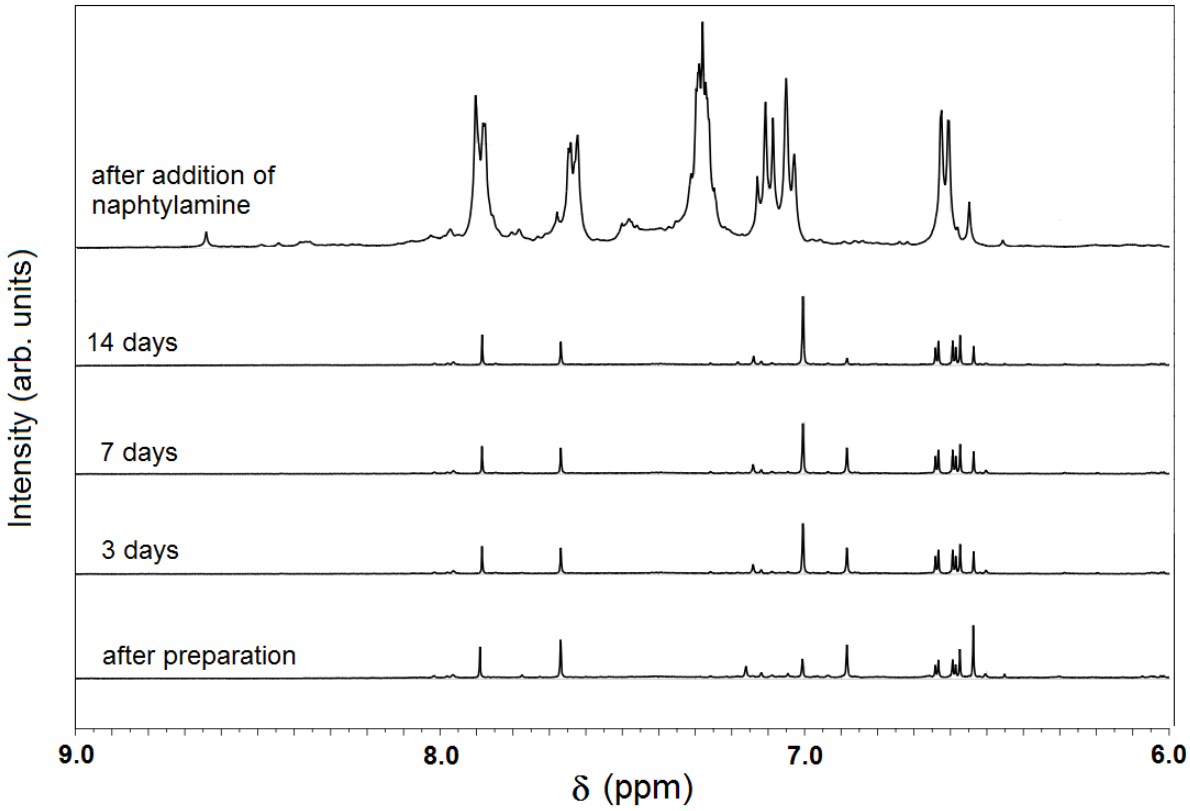

Figure 4: ^{1}H-NMR spectra of NA-Pt NPs in d_8-THF after preparation and during storage in THF. Upon storage no changes of the signals can be observed. After 14 days of storage, the same amount of NA as bound to the NPs was added to the sample. The rise of the signals indicates that the concentration of the sample is high enough to generate a significant NMR signal.

Furthermore, no signals arose that can be related to free naphthylamine. To confirm the absence of free ligands, ESI-MS (electrospray ionization mass-spectrometry) measurements were performed with the NA-Pt dispersions of catalytically activated samples. Since no naphthylamine was found in the solvent, we conclude that no ligands are removed from the ligand shell when NA-Pt NPs kept as colloids in THF. To probe changes in the ligand shell by NMR spectroscopy, it is prerequisite that the signals of bound ligands can be detected. Although the NMR sample contains a high concentration of

NA-Pt (ca. 0.06 mmol of bound NA), the proton signals in the aromatic region (6 – 8 ppm) are negligibly small. To verify that the sample concentration was sufficient for obtaining meaningful NMR signals, an equivalent quantity of pure ligand with respect to the concentration of the Pt NP bound ligands was added to the NMR sample. Strong signals of 1-naphthylamine arose immediately, which demonstrates that the concentration of Pt bound NA ligands is high enough to obtain meaningful NMR signals. For obtaining NMR signals from dissolved or dispersed samples it is prerequisite that the sample has unrestricted rotational mobility and diffusion within the solvent to ensure isotropic relaxation of the nuclear magnetization.[40] For dispersed ligand-functionalized NPs suitable motions are the diffusion of the particles in solution, rotation of the ligand on the surface, and internal rotational degrees of freedom of the ligand. As the diffusion of the particles in solution can be concluded to be too slow,[41] the appearance of NMR signals for ligand-functionalized NPs is limited to the presence of rotational motions of the surface bound ligands.[42] In contrast to e.g. alkyl amines, NA does not exhibit any internal rotational degrees of freedom.[8, 41] As a result, the only motion that could lead to the appearance of NMR signals is the rotation of surface bound NA along the metal-ligand bond. Due to its steric demand and the ability to establish strong lateral interactions with adjacent NA ligands (e.g. due to π-π stacking)[43-46] it must be assumed that this rotation is strongly inhibited. As a consequence, the appearance of ligand protons in the ^{1}H spectrum is diminished for surface bound NA ligands. In summary, NMR spectroscopy enables for excluding the escape of ligands from the ligand shell. In the present case it does however not reveal any evidence on processes that occur within the ligand shell, because the ligand shell of NA-functionalized Pt NPs cannot be probed by NMR spectroscopy.

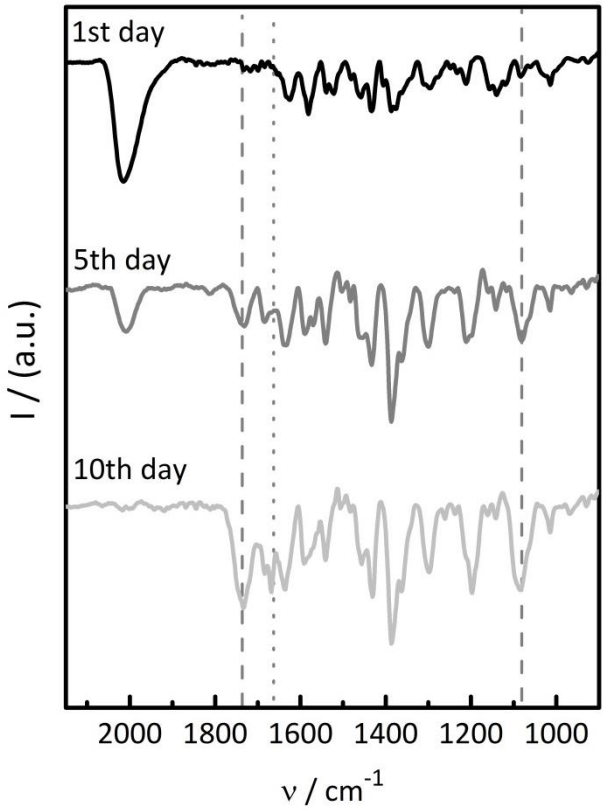

Figure 5: IR spectra of NA-Pt NPs on the first, fifth and tenth day of activation period. The vibration at around 1200 cm^{-1} can be attributed to the in-plane-bending of the CH groups in aromatic systems. However, the change of this vibration cannot be utilized to describe changes in the ligand structure.

IR spectroscopy was applied as an alternative method to probe changes in the ligand shell during activation. Figure 5 displays the IR spectra of the first, fifth and tenth day during NA-Pt activation. The vibrations of naphthylamine remain unchanged during activation, indicating that the ligand remains intact. Upon creation of ligand-free Pt ensembles, a shift of the CO vibration would be expected as CO adsorbed on adjacent surface sites leads to intermolecular CO dipole-dipole coupling.[33] The intensity and thus the amount of adsorbed CO were found to decrease over time, which evidences desorption of CO from the particle surface. The decreasing CO intensity is accompanied by the appearance and increase of two additional vibrations at 1726 cm^{-1} and 1081 cm^{-1} (see dashed lines in Fig. 5) that can neither be attributed to CO nor to naphthylamine. Comparison to unfunctionalized Pt NPs dispersed in THF (see Supplementary Information, Fig. S2 for IR spectrum of THF-Pt NPs) allows for assigning these vibrations to THF coordinated to Pt NPs. In addition, two vibrations arise around 1670 cm^{-1} (dotted line in Fig. 5). NA polymerizes readily in the presence of

catalytic materials.[47, 48] During polymerization of 1-naphthylamine, secondary amines (left reaction path in Fig.6) and imines (C=N-C, right reaction path in Fig. 6) are formed by a reaction between the NH_2 group and the hydrocarbon backbones.[20, 29]

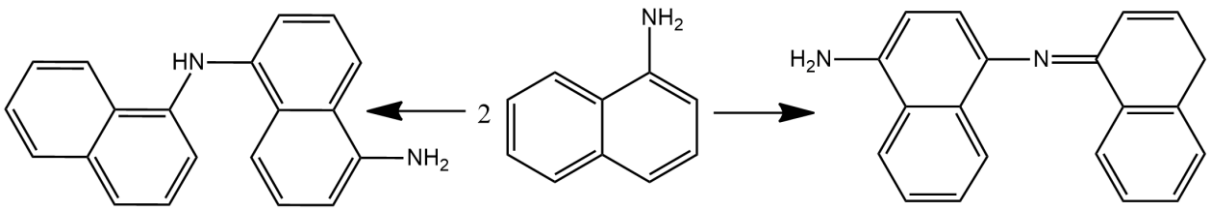

Figure 6: The two reaction pathways that proceed during polymerization of two 1-naphthylamine molecules according to Chung[20] and Ciric-Marjanovic.[29, 30] The left path leads to the formation of secondary amines, while the right reaction causes the formation of imines. In both structures the π-electrons are fully conjugated, leading to an extended delocalized electron system.

The latter leads to characteristic vibrations in a region from 1670-1658 cm^{-1}.[49] Upon coupling of NA monomers to oligo- or polymers, structures are formed in which all π-electrons are conjugated, leading to an extended, delocalized π-electron system. This enables for transferring charge over the polymer and thus to achieve redox reaction of the individual naphthyl-units.[20, 47] We hence propose that upon storing, NA ligands start to form oligomers, as visualized in Figure 7. In this way the electrocatalytic activity of the Pt sites can be generated, because ligands are removed from the particle surface. As the particles still form stable colloids in THF, the redox activity of the ligand is maintained, and H_{UPD} remains suppressed even after 10 days, it is concluded that the oligomer ligands remain adsorbed on the NPs.

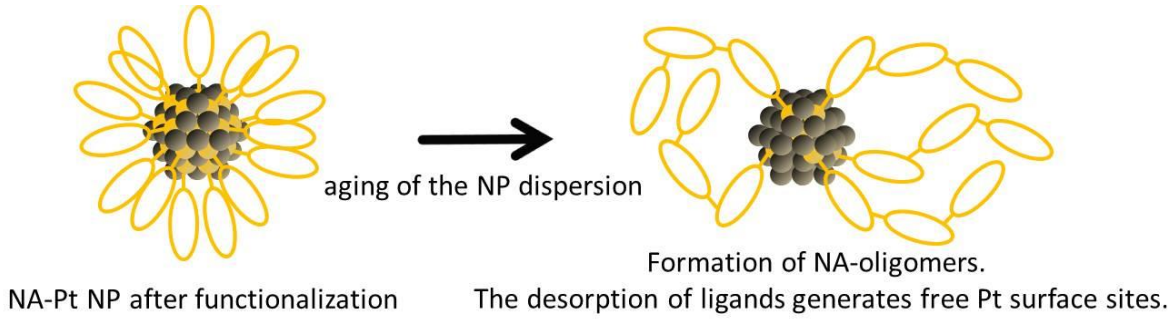

Figure 7: Storage of the NA-Pt NP dispersion and its effect on the ligand shell. We assume that during storage, the amine ligands may partially desorb from the Pt NP surface to form oligomers. In this way, adjacent Pt surface sites are created to allow for the electrocatalytic activity, while the redox properties of the ligands are partially maintained.

4. Conclusion

Pt nanoparticles (NPs) functionalized with 1-naphthylamine was introduced as a material that allows for electrochemically induced redox reaction of the NP bound ligand. Due to the high ligand density on freshly prepared naphthylamine-functionalized Pt NPs the electrocatalytic activity (e.g. CO stripping) on the Pt surface is suppressed as co-adsorption of the reactants on adjacent surface sites may be inhibited. However, after a catalytic activation pre-treatment, naphthylamine-functionalized Pt NPs can be activated for electrocatalytic reactions like CO stripping. Simultaneously, the redox activity of the naphthylamine ligands is maintained. Even though this indicates that ligand desorption occurs during the activation of naphthylamine-functionalized Pt NPs in tetrahydrofuran, no experimental evidence was found for the disappearance of ligands from the ligand shell. Instead, evidence was found that the ligands start to react with each other to form oligomers. These reactions cause the removal of surface bound ligands and thus lead to partial uncovering of the catalytic surface area, while the total ligand content of the material remains constant.

Our results demonstrate that bifunctional electrochemical systems can be prepared on the basis of ligand-functionalized NPs. In the present case, these two processes (ligand oxidation and catalytic reaction) occur successively. Therefore, no interference of the two was obtained. For future investigations it may be interesting to develop materials where the potential regimes of the two

reactions do significantly overlap. Maybe in this way it becomes feasible to achieve synergistic effects between the two processes.

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